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Agricultural Research Institute
PUSA

PROCEEDINGS

OF THE

ROYAL SOCIETY OF LONDON

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND
PHYSICAL CHARACTER.

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PROCEEDINGS OF

THE ROYAL SOCIETY.

SECTION A —MATHEMATICAL AND PHYSICAL SCIENCES

Discussion on the Electrical State of the Upper Atmosphere

(March 4, 1926)

SIR ERNEST RUTHERFORD During the last few years there have been a number of new lines of attack bearing on the problem of the constitution and electrical state of the upper atmosphere The work of Lindemann and Dobson on falling meteors has suggested that the pressure of the upper atmosphere calculated on the ordinary theory is seriously in error, and they conclude that the atmosphere above the isothermal layer of temperature about 220° A rises to about 300° A For heights of the order of 100 km the pressure may be 10 to 100 times the ordinary calculated value If these deductions are valid they must be taken into account in considering the amount of ionization at various heights due to the sun's rays, and of the ionization due to the very penetrating radiation in the atmosphere brought to light recently by the work of Kolhörster and Millikan

There is still some doubt as to the origin of this radiation, the intensity of which increases with height above the earth It may be, as Prof C T R Wilson has suggested, that it is of terrestrial rather than of cosmical origin, and may be due to the high velocity electrons and consequent radiation which should be present in strong electrical disturbances like thunderstorms No doubt the ionization in the upper levels is much increased by the " auroral " rays which extend down to about 100 km above the earth

The presence of a conducting region in the atmosphere, which on modern views is to be ascribed to ionization, has been postulated by Schuster and by Chapman in explanation of the diurnal variation of the earth's magnetism The passage of electrical waves round the earth early indicated the necessity of assuming a conducting or " Heaviside " layer, as it has been termed, in the upper atmosphere This view was given definiteness by the work of Eccles and others who showed that ionized gases could refract and absorb electrical waves passing through them This aspect of the question has been recently developed by Sir Joseph Larmor who has shown that the long free path of the electrons in the upper atmosphere is of paramount importance in producing scattering and refraction of radio-waves He has estimated that a comparatively sparse distribution of ions would be sufficient to bend the rays round the earth These calculations have been followed in the last year by new and successful experiments by Prof Appleton and Barnett and by Rose and Barfield, who have obtained convincing evidence that the waves are reflected or refracted at night time by a region in the upper atmosphere about 80 km in height for waves of about 400 metres in length These important observations have brought to light that the downcoming rays show marked polarization, effects no doubt connected with the action of the earth's magnetic field on the motion of the free electrons in the effective layer

The question arises whether the effects observed at night can be explained by the ionization of the upper atmosphere due to the penetrating rays and the auroral rays Taking into account that at low pressures the electron has a long life before being attached to a molecule and also the very slow recombination of the ions, the equilibrium number of ions in the upper atmosphere due to the penetrating radiation may easily amount to 10,000 per cubic centimetre or even higher It thus seems as if the ionization observed at night is of the right order of magnitude to fall in with the general observations of reflection or refraction of electrical waves at high altitudes, and may be of a magnitude also to explain the variations of the earth's magnetism I imagine the question is still *sub judice* whether the downcoming waves from the Heaviside layer are due to an actual refraction of the beam or to a type of specular reflection If the latter be true, it seems necessary to postulate a sharp increase of the total number of ions per cubic centimetre at a certain level in the atmosphere The efficiency of reflection will depend mainly on the number of free electrons and the length of their free path It may be that the actual concentration of electrons at night may at some points vary very rapidly with height due to the presence in the air of compounds formed in day time by the sun's ultra-violet rays. While recent research has shown that electrons liberated from helium nitrogen and oxygen have a long average life before becoming attached to a molecule, it is well known that small traces of impurities may have a great influence on the average free life of the electron. The presence, for example, of ozone or other compounds in the air may possibly have a large effect in this connection If this should prove to be the case, the amount of ozone in the atmosphere observed by Dobson may have a direct influence on its electrical state

The main discussion to my mind should centre round the following points —

(1) The mean free path of electrons and the rate of recombination of ions at various heights in the upper atmosphere

(2) The magnitude and origin of this ionization

(3) The amount and distribution of ionization required to explain the observations upon downcoming electric waves both as regards intensity and polarization

(4) Are the downcoming electric waves due to reflection or to refraction of the incident beam by an ionized layer ?

There can be no doubt that a continuation of the direct experiments, so successfully begun, for studying the propagation of electric waves in our atmosphere will give us most valuable information upon the subject of our discussion

Prof S Chapman Direct simultaneous measures of temperature and pressure up to 25 kilometres, by sounding balloons, give complete information as to the variation of pressure, density and temperature over this range The temperature falls in the first 10 km from 285° absolute to 220°, and then remains constant up to 25 or 30 km The temperature above this height was a subject merely for speculation until Lindemann and Dobson published their theory and discussion of meteors They concluded that the temperature remains at 220° up to 50 or 60 km , after which it rises (perhaps rather rapidly) to about 300°, which is its value up to about 140 km , thus at this height the air is warmer than near the ground This rise of temperature is inferred from the estimated densities of the air between 60 and 150 km , the density at 100 km being more than 10 times as great as it would be if the temperature had remained at 220° Higher up the difference between the estimated density and that calculated on the latter assumption is still greater The mean free molecular path, calculated on the assumption that the air is mainly nitrogen over this range, increases from about 1 cm at 90 km to about 10 cm at 130 km

Above this level, even if the temperature were fully known, the pressure and density could not be inferred without a knowledge of the composition, as to which, at present, there is much uncertainty In the lowest 10 km the air is thoroughly mixed by winds, but at some height H in the stratosphere diffusive separation may begin, the heavier constituents settling out so that the proportion of the lighter constituents steadily increases upwards Up to about 100 km.

the pressure and density do not depend much on H, but the composition is largely affected by it H = 20 km and H = 50 km would give very different results If we take H = 20 km as a likely value, nitrogen is still the main constituent at 100 km, its molecules being about 50 times as numerous as those of oxygen and helium Above 150 km there will be very little oxygen, and such lighter gases as are present (possibly helium and hydrogen) should be the main constituents

The question of the composition at 90 or 100 km is of interest in connection with the auroral spectrum The conditions there, in any case, are by no means those of a large excess of helium, as supposed by McLennan and Shrum in their discussion of the auroral spectrum The auroral spectrum shows that nitrogen and oxygen (accepting the identification of the green auroral line by McLennan and Shrum) are present at auroral heights At the lower auroral levels this is quite in accordance with expectation, but auroræ are said to appear up to heights of 500 km and more The evidence for this, given by Størmer and Vegard, seems quite satisfactory The presence of nitrogen and oxygen at such levels seems explicable only on the assumption that the atmosphere is partly supported at great heights by electrical forces, such as were discussed by Atkinson in his criticism of Vegard's theory of the aurora If such electrical forces operate, either permanently or merely temporarily when auroræ occur, they may have the effect of allowing the lighter gases, hydrogen and helium, to escape altogether, a suggestion which would, if substantiated, explain the rather remarkable absence of hydrogen and helium lines from the auroral spectrum, though a simpler explanation would be that mixing occurs up to auroral heights so that these gases occur only in the same minute proportions as in the lower atmosphere

Another matter of interest concerning the upper atmosphere is the highly conducting layer, the existence of which is indicated by the diurnal magnetic variation, according to the theory of Balfour Stewart and Schuster The conductivity of the layer must be of the order 3×10^{-6}, which is so great as to be difficult to explain But recently Appleton and Barnett have assigned 10^5 as a lower limit to the number of electrons per cubic centimetre at the level, about 80 km high, at which wireless waves are reflected at night From this it appears that the specific conductivity must be at least 3×10^{-14} c g s units at this height, a layer having this specific conductivity would require to be 1,000 km thick to account for the total conductivity 3×10^{-6} This excessive thickness can be reduced to a more reasonable figure, however, if the ionisation by day is several times as great as by night (as the diurnal magnetic variations themselves indicate), and if allowance is made for the increase in the mean free path above 100 km. The downward extension of the conducting layer, by day, into regions where the mean free path is less than at 100 km., may not add very much to the total conductivity. There seems no longer, however, any insuperable difficulty in supposing the thickness of the conducting layer to be of the order of 200 or 300 km., without assuming an excessive specific conductivity.

Prof. C. T. R. Wilson. Among the factors which determine the electrical state of the upper atmosphere thunderstorms may be by no means the least important. From a statistical study of the distribution of thunder storms* Mr. C. E. P. Brooks concluded that about 1,800 thunder-storms are on the average in progress at a given moment, producing about 100 lightning flashes per second. The quantity discharged in a flash† is of the order of 20 coulombs, and the potential difference which causes the discharge is of the order of 10^9 volts. Thus the power expended in producing lightning by all the thunder-clouds in action at a given time is of the order of 10^{12} watts or 10^{19} ergs per second, *i.e.*, about 1/10,000 of the energy received by the earth from the sun per second.

Not only is the electric power expended by thunder-clouds large, but each factor in the power (the current and the e.m.f.) has an order of magnitude which suggests the possibility of important effects on the electrical state of the upper atmosphere.

On the one hand, there is the possibility that thunder-clouds may supply to the upper atmosphere an upward current sufficient to maintain the positive potential difference (of the order of 10^6 volts as shown by measurements of the potential gradient in fine weather regions) which exists between the upper atmosphere and the earth, and to balance the downward current which flows in the fine weather regions in consequence of this potential difference (of the order of 1000 amperes for the whole earth).

Again the large e.m.f. of a thunder-cloud is likely to make it act as a source of β-rays and of X and γ-radiations of energies ranging from 10^4 to 10^9 volts,‡ *i.e.*, up to values exceeding the energy of the hydrogen nucleus and corresponding to the most penetrating type of radiation that has been imagined. For a particle of energy exceeding about 10,000 volts will, in general, gain in the strongest part of the field of a thunder-cloud (if moving approximately along the direction of the force) more than sufficient energy per cm. to make up for that lost in encounters; and when it has acquired energy exceeding a few hundred thousand volts the loss of energy per cm will be of the order of 1,000 volts only and thus small compared with that derived from the field If the acceleration not only of the primary β-rays but of the secondary and higher order β-particles, ejected by those which have already been accelerated, be taken into account it is easily seen that the energy spent in producing penetrating corpuscular and γ radiation may be large—possibly approaching that which is expended in producing lightning discharges

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* C. E. P. Brooks, Meteorological Office, 'Geophysical Memoirs,' 24.

† C. T. R. Wilson, 'Phil. Trans.,' A, vol. 221, p. 73 (1920).

‡ C. T. R. Wilson, 'Proc. Camb. Phil. Soc.,' vol. 22, p. 534 (1925).

Penetrating β-rays from thunderclouds may traverse the upper atmosphere, and under the influence of the magnetic field re-enter the atmosphere in widely scattered regions, contributing perhaps to auroral phenomena and to the penetrating radiation, studied by Kolhörster and recently by Millikan, to which a cosmical origin has generally been assigned

SIR HENRY JACKSON Systematic measurements of the variations in the intensity and the direction of signals received from Radio telegraph stations have been taken for some years by skilled observers, and their analysis showed clearly they were subject to seasonal, diurnal and other effects, and that the Sun's altitude had a great effect on them, but nothing more definite than this was obtained

However, in considering the effect of electro-magnetic waves on a wireless receiver it was deduced that the variations could be accounted for if two or more waves from the same source and of the same frequency reached the receiver simultaneously but at different phases of their oscillations, and, for some of the effects in directional work, if one of them was polarized in a different plane to the others

The fading effects noticed with short waves can also be attributed to the same causes

The recently published work on the Kennelly-Heaviside layer theory was studied, and experiments carried out to try if deflections and conduction by some such agency as this layer could be detected and measured Several observers have been successful in doing this, by different methods, and their collective results, published independently, go far, I think, to establish the validity of the idea

There are, however, many calls upon this layer which require consideration to account for all the varying results that are now obtained in Radio communications which cannot be attributed to locality, apparatus or to personnel.

The variations experienced with long waves are well known, but with very short waves, say under 100 metres, another phenomenon is noticed, and, with

Admiralty permission I will quote a very recent example of this and observe this is not an effect that can be attributed to two waves at different phases affecting the receiver

A vessel on a long voyage transmits a 12 metre wave every 4 hours and also other wave lengths at stated periods under a carefully organised programme The 12 metre signals were received by a station near her port of departure during the first hundred miles of her voyage then lost altogether till she reached 1 100 miles then heard occasionally during daylight up to about 4 500 miles then lost till she reached the end of her voyage 6 000 miles when a very clear signal was again received The small loss of signal strength if any at this distance is noticeable and many other observations on these short waves confirm this though signal strength varies enormously but not necessarily decreasing much with distance A longer wave (nearing 100 metres) was received from the same vessel up to 1 000 miles then lost and only heard twice during the remainder of the voyage Three other waves intermediate between these are received intermittently during some part of the day and communication has been maintained with these during the whole voyage

Fading is often very prominent with all these short waves and at times double fading is noticed *i e* a short period of small amplitude superposed on one of long period with large amplitude Distortion of long dashes causing an audible wave of varying pitch and intensity and also the missing of short dots are also noticeable

These results indicate that the layer must exercise but little attenuation on short waves which show small loss of energy in their passage along it and that it appears to deflect down some wave-lengths at various places some distance apart and others possibly at all points on the earth s surface and that two or more waves must sometimes reach the receiver at varying and different phases of their oscillations to account for the extraordinary fading effects that are so often noticed with them

Is a layer that will fulfil all these functions a physical possibility ? If not, what is the cause of these variations ?

Prof E V Appleton In attempting to obtain information about the electrical state of the upper atmosphere from wireless data it is found that the evidence obtained from short distance transmissions is much more direct and much more easily interpreted than is that from transmissions over longer distances The reason for this is two fold In the first place, by studying the deviation of wireless rays through large angles by the atmosphere we are able to estimate very directly the electron-concentration of the ionized layer. Secondly, in short distance transmissions, there is, in most cases, a ground ray arriving at the receiving station, which, acting as a reference ray, enables us to study the amplitude and phase of rays reaching the receiver via the atmosphere.

During the last few years two experimental methods,* specially suitable for investigating the upper atmosphere by means of short-distance transmissions, have been developed at Cambridge. The application of these methods yielded a direct experimental proof of the existence of the ionized layer. In the first type of experiment the wave-length of a transmitter was changed continuously through a small range, and the interference maxima and minima were observed at a receiving station 80 miles away. This experiment showed that signal "fading," at such distances, was due to the interference of two or more sets of waves arriving at the receiving station, and also gave an estimate of the path differences between them. To prove that the interfering rays came down from the upper atmosphere methods of examining the electric and magnetic forces in the stationary wave system at the ground were employed. By comparing the signal variations produced on a loop and on a vertical antenna at the same time and place, it was possible to measure the angle at which the downcoming rays reach the ground. From the results of such experiments we may estimate (*a*) the height of the ionized layer, (*b*) the relative intensities of the ground and atmospheric rays, (*c*) the "reflection coefficient" of the ionized layer, and (*d*) the state of polarization of the atmospheric rays.

The study of atmospheric influences on ultra-short wave transmission leads to a theory of imprisoned and escaping rays and wave-lengths. Due to the finite electronic content of the ionized layer, wave-lengths less than a certain critical value are not bent back to the earth and escape via the atmosphere. Further, only certain rays of wave-lengths slightly higher than the minimum wave-length are bent back. An interpretation of these phenomena gives 10^5 — 10^6 as the order of magnitude of the maximum number of electrons per cubic centimetre in the layer.

The rays deviated by the atmosphere have been examined and found to be in general elliptically polarized, as is to be expected according to the magneto-ionic theory. This theory shows that the effect of the earth's magnetic field causes the atmosphere to act like a quartz crystal, in that rotation of the plane of polarization takes place for transmission along the axis and double refraction for transmission at right angles An examination of the expressions for the refractive index and the absorption coefficient for such cases shows, as one would expect, that the influence of the magnetic field is most marked when the mean free path of the electron is large, so that we have here a satisfactory explanation of night-time directional errors

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* Appleton and Barnett, 'Nature,' March 7, 1925; 'Roy. Soc. Proc.,' A, vol. 109, p. 621 (1925).

Thus, summarizing, we find that wireless phenomena demand the existence of an ionized layer, the maximum electron concentration of which is 10^5-10^6 per cubic centimetre The ionized layer deviates very long waves by reflection, because the change of conductivity is sufficiently sharp within a wave-length, and deviates short waves by magneto ionic refraction In the latter case, to account for low attenuation one must assume, as Larmor first pointed out, that the frequency of the waves is less than the frequency of the electron collisions with the molecules Diurnal variations of wireless phenomena all seem to be explicable by assuming that the under boundary of the effective stratum is higher at night than during the day, and higher in winter than in summer The evidence so far obtained indicates a day-time under-boundary at 50 to 70 km, which rises to 80 to 120 km at night

Dr R L SMITH-ROSE (with Mr R H BARFIELD) In the March issue of the Proceedings of the Society* a paper was published by us which described in some detail a theoretical and experimental investigation of wireless waves as received on the earth's surface It was first of all shown in this paper that for waves arriving at an inclined angle to the earth's surface, the directions of the electric and magnetic forces resulting from the combination of incident and reflected waves should depart from the normal directions of these forces in the case of waves propagated horizontally along the earth's surface From experiments described in a previous paper† it was found that on wave-lengths above 1,000 metres, and owing to the high conductivity of the earth, these departures were so small as to make it impossible to distinguish between horizontally propagated waves and those arriving in a downward direction Later experiments, carried out on wave-lengths of about 400 metres have, however, given more definite and interesting results The results obtained are described in the recent paper referred to above, and prove that at times in the neighbourhood of sunset and in the hours of darkness, some of the received waves were travelling in a downward direction, evidently the result of deflexion from the upper atmosphere Simultaneously with these experiments a method

* 'Roy Soc Proc.,' A, vol 110, p 580 (1926)

† 'Roy. Soc. Proc,' A, vol 107, p. 587 (1925)

of measuring the instantaneous relative intensities of the electric and magnetic forces at the earth's surface was developed This method, which is very similar in nature to that just described by Prof Appleton and Mr Barnett, also gave direct proof of the existence of downcoming waves A combination of these experiments provided several methods of measuring the angle of incidence and relative intensities of these waves, and these were found to give mutually consistent results In an example cited in the paper, the angles of incidence varied from 13° to 34°, and the latter value is shown to correspond to a height of deflecting layer of about 88 km which is in good agreement with the results of other investigators The intensity of the downcoming waves was found to be of the same order as the direct wave along the earth's surface which was received simultaneously

Further investigation on this matter is desirable since it will undoubtedly lead to a greater knowledge of the physics of the upper atmosphere With the object of obtaining more definite results we propose to carry out experiments with a concentrated beam of radiation projected at definite angles of incidence towards the upper atmosphere, and to locate and investigate the deflected waves on their return to the earth's surface Practical considerations necessitate that this work should be carried out on shorter wave-lengths, and the preliminary experimental work is already in progress

Prof W H Eccles Preceding speakers having marshalled the available evidence for the Heaviside layer, it may be most useful for me, while agreeing broadly with the conclusions drawn from that evidence, to refer to some other points of view and other agencies For instance, in connection with wireless phenomena at short distances from the transmitting station, the diminution of the density of the air with increase of height, which causes the lower atmosphere to act as a prism with its base on the ground, taken together with diffraction, must not be ignored Consider a source from which electric waves of length 20 metres, 600 metres and 20,000 metres are being simultaneously emitted, and consider especially the rays emitted horizontally Up to distances of 100 km. all these waves can be detected by an ordinary aerial—beyond that distance the 20 metre waves vanish but the others remain perceptible This, I suggest, indicates diffraction of the longer waves, as is supported by the fact that an aerial on a high mast or hill can detect the short waves passing aloft like the beam of a searchlight I want to suggest also that variations of signal strength at these short distances may be due to variations in or movements of the lower atmosphere. (The well-known vertical oscillations of pilot balloons at a height of 10 km suggest movements of the air)

Beyond 100 km in daylight the 20 metre signals are completely lost the others are continuously perceptible It has been found (e g by Hollingworth) that after falling off with distance the long wave signals increase up to a distance of 400 km Here it seems that the ionized atmosphere is aiding diffraction and the prismatic action At 700 km the lost 20 metre signals reappear though the tangent plane through the source passes 100 km above This suggests that the horizontal rays from the source have followed a trajectory perhaps only 30 km in height at its apex and now graze the ground again Rays starting with an upward angle from the source would on this view descend to earth at greater distances and perhaps at grazing incidence These possibilities have caused me to remain unconvinced by Prof Appleton s use of the skip of short waves to deduce the maximum electron density at a sharply defined Heaviside surface nearly 100 km high This possible explanation by aid of non intersecting and gradually bending trajectories of varying height demands considerable thickness in the Heaviside layer It is perhaps in disaccord with Sir Joseph Larmor s recent review of an old theory for he appears to doubt ionic bending in the lower atmosphere and supports the whispering gallery view which assumes the formation of a thin caustic layer of radiation in the sky

The preceding remarks refer to daytime propagation At night the 20 metre waves make a larger skip say 4 000 miles and are picked up at all distances beyond the 600 metre waves are picked up at all distances to 5 000 miles and the 20 000 metre waves go everywhere Measurements are available on the medium wave lengths and show that in the great fluctuations of strength beyond 2 000 miles the maximum may exceed the strength calculated for a perfectly conducting flat earth with a non absorbing atmosphere This seems one of the best proofs of the existence of the Heaviside layer for otherwise we must believe that the earth is flat

Dr G M B Dobson The evidence obtained from radio telegraphy indicates that the upper atmosphere at a height of some 50 to 80 km is considerably ionized or may contain a moderate number of free electrons We shall see that there is evidence of an entirely different nature which supports such a view

Large numbers of meteors have been observed by Mr Denning and his associates If the frequency with which meteors appear at any height be examined, it is found that the most frequent height for a meteor to appear is about 110 km and the number decreases regularly above and below this level When, however the height of disappearance is plotted we find that the main maximum occurs at 80 km. but that a secondary maximum also occurs at 45 km, with a region between 50 km and 60 km, where very few meteors disappear Any errors of observation would tend to smooth out this minimum frequency, and that its existence is shown at all is an indication of the accuracy of the observations All the meteors dealt with are of similar character, and there is no evidence that the two maxima are due to two types of meteor

The only suggestion which would seem to account for this type of frequency curve is that the atmosphere above and below 60 km is different From other considerations of meteor observations, we have evidence that while the air up to 50 km has a temperature of about 220° A, that above 60 km has a much higher temperature The observed minimum of frequency may be explained by this change of temperature

We know that ozone is formed from oxygen by the action of ultra-violet light of wave-lengths shorter than about 1800 Å, so that we should expect that it would be formed in the upper layers of the atmosphere by sunlight Owing to the rapid absorption of these short waves, it is probable that the ozone would be formed chiefly at a height of about 50 km.

Prof Lindemann has pointed out, that while other constituents of the atmosphere are nearly transparent to the wave-lengths emitted by the sun, and have absorption bands only in the infra-red, ozone has absorption bands both in the visible and ultra-violet regions, and hence its radiation equilibrium temperature will be relatively high Thus we should expect the highest layers of the atmosphere where ozone is present to be warmer than those below, as has been indicated by meteor observations

In addition to forming ozone, the sun's ultra-violet light will ionize the air, and produce the conducting layer indicated by radio observations

Again, Dr Chree has shown that days on which much ozone is present, are associated with high magnetic character, which may be due to the increased ionization Measurements of the amount of ozone to be made shortly at Chile, where the results should not be disturbed by changes connected with variations of barometric pressure, will afford interesting comparison with magnetic data

Dr G C SIMPSON The country has every reason to be proud of the work just described, for it is of fundamental importance to our knowledge of the upper atmosphere I think there is no doubt that Britain now leads the world in this branch of knowledge and research We are pleased that Sir Arthur Schuster should be present to hear of the later developments of the work which he started so long ago

Prof F A LINDEMANN I was much interested in Prof C T R Wilson s suggestion that 1 000 million volt electrons might be obtained from lightning discharges If this somewhat startling idea proves to be true and it should be easily susceptible of verification, it would introduce a new and potent factor into geophysical speculation I can scarcely believe however that it can account for the ionisation in the upper air which the discussion we have just heard seems to force us to accept If the major part of the current which Prof Wilson attributes to lightning were to appear in the form of such electrons they might if highly efficient produce enough ions but it seems inconceivable that they should produce them all above a certain height as is necessary to account for the wireless phenomena

The main problem namely to explain the production of the required ionisation therefore remains In daytime it is simple enough for it can be attributed to solar ionisation This explanation breaks down at night when most of these experiments were made To attribute them to electrical effects such as auroræ seems fanciful since these occur very much higher up and are much too erratic to account for such a regular phenomenon as the Heaviside layer Ions caused by sunlight could scarcely persist in sufficient numbers at heights so low as are demanded The only suggestion I have heard which does not seem impossible on the face of it was mentioned to me by Mr R d E Atkinson He pointed out that the persistence of ionization through the night would be accounted for if the ozone produced by the sun s radiation broke up into ions In this case the ionisation would be maintained as long as there was ozone to break up The layer would gradually ascend as the night progressed since recombination would take place most rapidly at high pressures Finally if Dr Dobson and I are right in our view that there is a sudden rise in temperature between 50 and 60 km it would be natural that there should be ionization mainly above this height For the rate of decomposition of ozone would be negligible in the cold region at 220° between 11 and 50 km but would be considerably greater at the temperatures about 300° which we believe to obtain above 60 km The whole hypothesis of course stands and falls with the assumption that ozone breaks up into ions accurate experiments on this question seem most desirable

On Wave Resistance.

By HORACE LAMB, F R S

(Received February 27, 1926)

The case here considered is that of a solid whose dimensions are small compared with its depth below the free surface, travelling horizontally under water The particular case of a circular cylinder advancing at right angles to its length was easily solved from considerations of group-velocity[*] The more difficult problem of the sphere was worked out by Havelock[†] by direct calculation of the pressures exerted on its surface In a subsequent paper[‡] this rather arduous process was avoided by a calculation of the travelling pressures, applied to the free surface, which would produce the same wave system The work done by these must be equivalent to that which, in the actual case, is expended on the sphere to maintain its motion The same principle was further employed by him to find the wave-resistance of other solids of revolution, in particular that of a spheroid

There would appear to be room for an investigation on a more general plan in which no restriction is made as to the form of the solid, which affects only the values to be attributed to certain constants (familiar in another connection) in the final results *For example, it is not necessary even to assume that the* solid is moving in one of the directions of free " permanent translation " of which it is capable, and some attention is paid to cases where this condition is departed from As a further variation from previous methods a small viscous force is introduced, and the work done against resistance is equated to the dissipation of energy

1 The velocity-potential at any point P in an unlimited mass of liquid, due to the motion of a solid through it, is expressed in terms of a distribution of double sources over the surface of the solid by the formula

$$4\pi\phi_P = \iint (\phi - \phi') \frac{\partial}{\partial n} \frac{1}{r}\, dS, \qquad (1)$$

where r denotes the distance of P from a surface-element δS, and the differentiation $\partial/\partial n$ is in the direction of the outward normal The auxiliary function ϕ' is the velocity-potential of a fluid imagined to occupy the same space as the solid, and to be confined by a thin rigid envelope coincident with the boundary, where accordingly

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[*] 'Ann di matematica,' vol 21, p 237 (1913), 'Hydrodynamics,' Arts. 247, 249

[†] 'Roy Soc. Proc,' vol. 91, p 520 (1917)

[‡] 'Roy. Soc Proc,' vol. 93, p 354 (1918)

$$\frac{\partial \phi'}{\partial n} = \frac{\partial \phi}{\partial n} \tag{2}$$

To evaluate (1) at points whose distance is large compared with the dimensions of the solid, we take an origin in the interior, say at the mean centre, and denote by (x_1, y_1, z_1) the co-ordinates of P, and by (x, y, z) those of a surface element δS Then, writing

$$r_1 = \sqrt{(x_1^2 + y_1^2 + z_1^2)},$$

we have

$$\frac{1}{r} = \frac{1}{r_1} + \frac{x x_1 + y y_1 + z z_1}{r_1^3} + \tag{3}$$

Hence,

$$\frac{\partial}{\partial n}\frac{1}{r} = \frac{l x_1 + m y_1 + n z_1}{r_1^3}, \tag{4}$$

approximately, where (on the right-hand side) l, m, n are the direction-cosines of the normal to δS, drawn outwards

Suppose, now, that the solid is moving with unit velocity in the direction Ox, without rotation We have then

$$\iint \phi \frac{\partial}{\partial n}\frac{1}{r}\, dS = \frac{A x_1 + C' y_1 + B' z_1}{r_1^3}, \tag{5}$$

where

$$A = \iint \phi l \, dS, \quad C' = \iint \phi m \, dS, \quad B' = \iint \phi n \, dS \tag{6}$$

These quantities A, C′, B′ are recognized as inertia-coefficients occurring in the general expression for the energy of an infinite mass of liquid of unit density due to the translation of a solid through it with velocity (u, v, w), viz *

$$2T = Au^2 + Bv^2 + Cw^2 + 2A'vw + 2B'wu + 2C'uv \tag{7}$$

Again, on the present supposition we have

$$\phi' = -x, \tag{8}$$

and therefore, from (4),

$$-\iint \phi' \frac{\partial}{\partial n}\frac{1}{r}\, dS = \frac{Q x_1}{r_1^3}, \tag{9}$$

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* 'Hydrodynamics,' Art 121

where Q denotes the volume of the solid, since

$$\iint xl\, dS = Q, \quad \iint xm\, dS = 0, \quad \iint xn\, dS = 0 \tag{10}$$

Hence, finally,

$$4\pi\phi_P = \frac{(A + Q)\, x_1 + C'y_1 + B'z_1}{r_1^3} \tag{11}$$

The effect of the motion of the solid at distant points is therefore that of a double source, but the axis of the source does not necessarily coincide with the direction of the translation, which has been assumed to be that of the axis of x

If, however, the axis of x coincides with one of the three mutually perpendicular directions of permanent translation* of which the solid is capable, the coefficients C′ and B′ will vanish In what follows it is assumed in the first instance that this is the case Then

$$4\pi\phi_P = (A + Q)\, x_1/r_1^3 \tag{12}$$

2 Proceeding now to the wave problem, we take the origin of co ordinates in the free surface of the fluid and the axis of z vertically upwards The solid will be supposed to move in the zx plane with velocity c in the *negative* direction of x, at a depth f

If we introduce a small frictional force varying as the velocity the pressure-equation is

$$\frac{p}{\rho} = \frac{\partial\phi}{\partial t} + \mu\phi - gz, \tag{13}$$

terms of the second order in the velocity being neglected Hence, if ζ denotes the surface-elevation we have, for $z = 0$,

$$g\zeta = \frac{\partial\phi}{\partial t} + \mu\phi, \quad \frac{\partial\zeta}{\partial t} = -\frac{\partial\phi}{\partial z} \tag{14}$$

These conditions are satisfied by

$$\zeta = e^{\alpha t}\chi(x, y), \quad \phi = Ce^{\alpha t + kz}\chi(x, y), \tag{15}$$

where $\chi(x, y)$ is any solution of

$$\frac{\partial^2\chi}{\partial x^2} + \frac{\partial^2\chi}{\partial y^2} + k^2\chi = 0, \tag{16}$$

provided

$$(\alpha + \mu)\, C = g, \quad kC = -\alpha \tag{17}$$

Hence,

$$\alpha = -\tfrac{1}{2}\mu \pm i\sigma, \quad \text{where } \sigma = \sqrt{(gk)}, \tag{18}$$

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* 'Hydrodynamics,' Art 124

the square of μ being neglected In particular, the free waves consequent on an initial state

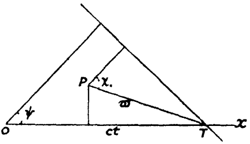
$$\zeta = \chi(x, y), \quad \partial\zeta/\partial t = 0 \tag{19}$$

are given by

$$\phi = \frac{\sigma}{k} e^{-\frac{1}{2}\mu t + kz} \sin \sigma t \, \chi(x, y), \tag{20}$$

$$\zeta = e^{-\frac{1}{2}\mu t}\left(\cos \sigma t + \frac{\mu}{2\sigma} \sin \sigma t\right) \chi(x, y) \tag{21}$$

3. In the annexed figure positions of the solid are indicated by their vertical projections on the free surface Thus, the origin O represents the position at



the instant for which the value of ϕ is required, whilst T corresponds to the position at some antecedent time t, so that OT $= ct$

If the solid had been suddenly started from T with velocity c towards O, everything being previously at rest, the consequent value of ϕ would have been, to a first approximation,

$$\phi = \mathrm{H} \frac{\partial}{\partial x} \frac{1}{r} \tag{22}$$

where r denotes distance from the centre of the solid, and

$$\mathrm{H} = (\mathrm{A} + \mathrm{Q})\, c/4\pi \tag{23}$$

by (12) Since f denotes the depth of the solid, we have

$$r^2 = (z + f)^2 + \varpi^2, \tag{24}$$

where ϖ denotes distance from T in the horizontal plane

Since

$$\frac{1}{r} = \int_0^\infty e^{-k(f+z)} \mathrm{J}_0(k\varpi)\, dk, \tag{25}$$

the formula (22) becomes

$$\phi = \mathrm{H}\int_0^\infty e^{-k(f+z)}\frac{\partial}{\partial x}\mathrm{J}_0(k\varpi)\,dk \tag{26}$$

To correct this for the influence of the free surface, where ϕ must $=0$, we add

$$-\mathrm{H}\int_0^\infty e^{-k(f-z)}\frac{\partial}{\partial x}\mathrm{J}_0(k\varpi)\,dk, \tag{27}$$

and obtain, for the initial surface velocity

$$\frac{\partial\zeta}{\partial t} = -\frac{\partial\phi}{\partial z} = 2\mathrm{H}\int_0^\infty e^{-kf}\frac{\partial}{\partial x}\mathrm{J}_0(k\varpi)\,k\,dk \tag{28}$$

4. Now suppose that, everything being at rest to begin with, the solid (at T) is suddenly moved from rest to rest through an infinitesimal step $c\delta t$ towards O The nett result of this will be to leave the surface initially at rest, but with an elevation

$$\zeta = 2\mathrm{H}\,\delta t\int_0^\infty e^{-kf}\frac{\partial}{\partial x}\mathrm{J}_0(k\varpi)\,k\,dk \tag{29}$$

Hence, comparing with (20) and (21), the subsequent history of the surface would be given by

$$\phi = -2i\mathrm{H}\,\delta t\int_0^\infty e^{-kf-\frac{1}{2}\mu t+i\sigma t}\frac{\partial}{\partial x}\mathrm{J}_0(k\varpi)\,\sigma\,dk \tag{30}$$

provided the real part only be retained in the end

Since

$$\mathrm{J}_0(k\varpi) = \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{-ik\varpi\cos\chi}\,d\chi, \tag{31}$$

the motion represented by (30) may be regarded as made up of rectilinear wave-trains whose directions of propagation are distributed in azimuth about T Now, referring to the figure, the distance of any point P of the free surface, whose co-ordinates are x, y, from a rectilinear wave-front through T will be

$$(ct - x)\cos\psi - y\sin\psi$$

where ψ is the angle which the normal to the wave-front makes with Ox This expression takes the place of $\varpi\cos\chi$ in (31), and since the integrand is periodic with respect to χ, with the period 2π, whilst χ differs only from ψ by a constant, we may replace χ by ψ as independent variable, with the same range of integration Thus,

$$\phi = \frac{\mathrm{H}\,\delta t}{\pi}\int_0^\infty\int_{-\pi}^{\pi} e^{-kf-\frac{1}{2}\mu t+i\sigma t+ik\{(x-ct)\cos\psi+y\sin\psi\}}\,\sigma k\,dk\cos\psi\,d\psi \tag{32}$$

Regarding the travel of the solid from infinity to the position O as made up of such infinitesimal steps $c\delta t$, we integrate with respect to t from 0 to ∞, and obtain

$$\phi = \frac{H}{\pi}\int_0^\infty\int_{-\pi}^{\pi}\frac{e^{-kf+ik(x\cos\psi+y\sin\psi)}}{\frac{1}{2}\mu - i(\sigma - kc\cos\psi)}\,k\sigma\,dk\cos\psi\,d\psi \tag{33}$$

as the surface-value of ϕ at the instant required

The interpretation of this result by approximate methods has been explained elsewhere[*] As regards the integration with respect to k, the more important elements are those for which k differs little from the value (κ) which makes $\sigma = kc\cos\psi$ Since we are concerned only with positive values of k, this implies that $\cos\psi > 0$ Hence writing $k = \kappa + k'$, where

$$\kappa = g/c^2\cos^2\psi, \tag{34}$$

we have, for small values of k',

$$\tfrac{1}{2}\mu - i(\sigma - kc\cos\psi) = \tfrac{1}{2}\mu - i(U - c\cos\psi)\,k', \tag{35}$$

where U is the group-velocity corresponding to the wave-velocity $c\cos\psi$, or $U = \frac{1}{2}c\cos\psi$ This gives

$$\phi = \frac{2H}{\pi}\int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi}\left\{\int_{-\infty}^{\infty}\frac{e^{ik'q}}{\mu + ik'c\cos\psi}\,dk'\right\}e^{-\kappa f+i\kappa q}\,\kappa^2 c\cos^2\psi\,d\psi, \tag{36}$$

approximately, where $q = x\cos\psi + y\sin\psi$ The limits of ψ have been here contracted to $\pm\frac{1}{2}\pi$, since $\cos\psi$ must be positive, whilst those of k' have been extended to $\pm\infty$, since owing to the fluctuation of the periodic term only mutually destructive elements are, on the whole, thus introduced Now, by a known theorem we have

$$\int_{-\infty}^{\infty}\frac{e^{ixq}}{a + ix}\,dx = 2\pi e^{-aq},\quad\text{or}\quad 0, \tag{37}$$

according as $q \gtrless 0$ Hence

$$\phi = \frac{4Hg^2}{c^4}\int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} e^{-\kappa f+(i\kappa-\mu_1)q}\sec^3\psi\,d\psi, \tag{38}$$

where

$$\kappa = g/c^2\cos^2\psi,\quad \mu_1 = \mu/c\cos\psi,\quad q = x\cos\psi + y\sin\psi, \tag{39}$$

provided $q > 0$ If $q < 0$, the result is negligible, on the present approximation.

The integral in (38) can be approximated to by Kelvin's method[†] We write

$$F(\psi) = \kappa q = \frac{g(x\cos\psi + y\sin\psi)}{c^2\cos^2\psi}, \tag{40}$$

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[*] 'Phil. Mag.,' vol. 31, p. 539 (1916)

[†] 'Roy Soc. Proc.,' vol. 42, p 80 (1887); 'Math. and Phys. Papers,' vol. 4, p. 303

Owing to the fluctuations of the periodic factor ($e^{i\varpi}$) in the integral, the most important elements are those for which the argument is nearly stationary Hence, putting $\psi = \theta + \omega$, where θ is a root of $F'(\theta) = 0$, and therefore

$$F(\psi) = F(\theta) + \tfrac{1}{2}\omega^2 F''(\theta) + \quad , \tag{41}$$

the variation of ψ in the remaining factors of the integrand may be neglected, and the limits of ω may at the same time be extended to $\pm\infty$ without serious error. Now from (40) we have

$$\frac{F'(\psi)}{F(\psi)} = \frac{-x \sin\psi + y \cos\psi}{x \cos\psi + y \sin\psi} + 2\,\frac{\sin\psi}{\cos\psi}, \tag{42}$$

and therefore, since $F'(\theta) = 0$,

$$\frac{F''(\theta)}{F(\theta)} = 1 - 2\tan^2\theta \tag{43}$$

If we put

$$|\tfrac{1}{2} - \tan^2\theta|\, F(\theta) = m^2, \tag{44}$$

the value of ϕ is reduced to depend on the integral

$$\int_{-\infty}^{\infty} e^{\pm i m^2\omega^2}\, d\omega = \frac{\sqrt{\pi}}{m}\, e^{\pm\frac{1}{4}i\pi}, \tag{45}$$

where m is of course to be taken positively We obtain finally

$$\phi = \frac{4\sqrt{\pi} g^2 H e^{-\kappa f}}{c^4 m} \sec^3\theta \;\; e^{i\{\kappa(x\cos\theta + y\sin\theta) \pm \frac{1}{4}\pi\}} \;\; e^{-\mu_1(x\cos\theta + y\sin\theta)}, \tag{46}$$

where, now,

$$\kappa = g/c^2 \cos^2\theta, \quad \mu_1 = \mu/c\cos\theta, \tag{47}$$

and θ is determined as a function of x, y by the equation $F'(\theta) = 0$, or

$$x\tan\theta + y(1 + 2\tan^2\theta) = 0 \tag{48}$$

We have also the proviso

$$x\cos\theta + y\sin\theta > 0 \tag{49}$$

The equation (48) shows that there are two values of $\tan\theta$ within the range of ψ, provided $x^2 > 8y^2$ Since their product is $\frac{1}{2}$, one value will be numerically less, and the other numerically greater, than $\tan^{-1}\dfrac{1}{\sqrt{2}}$ The sign to be attributed to $\frac{1}{4}\pi$ in (46) will be $+$ in the former case and $-$ in the latter.

It is now convenient, adopting a suggestion of Kelvin,* to write

$$x\cos\theta + y\sin\theta = a\cos^2\theta, \tag{50}$$

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* 'Math. and Phys. Papers,' vol. 4, p. 413

and to regard the position of a point (x, y) as determined by the two parameters a and θ Taking (48) in conjunction with (50) we have

$$x = a\cos\theta\,(1 + \sin^2\theta), \qquad y = -a\sin\theta\cos^2\theta \tag{51}$$

It appears from (49) that a must be positive The equations just written show that the two values of $\tan\theta$ will be positive in that quadrant of the plane in which x is positive and y negative On account of the symmetry with respect to the axis of x we may confine our attention to this quadrant The two values of θ may be then taken to lie between 0 and $\frac{1}{2}\pi$ Denoting them by θ_1, θ_2, and the corresponding values of a by a_1, a_2, we have

$$\phi = \phi_1 + \phi_2$$

where

$$\phi_1 = \frac{4\pi^{\frac{1}{2}}g^{\frac{1}{2}}\mathrm{H}\sec^3\theta_1}{c^3 a_1^{\frac{1}{2}}\sqrt{(\frac{1}{8} - \tan^2\theta_1)}}\, e^{-\frac{gf}{c^2}\sec^2\theta_1 - \mu\frac{a_1}{c}\cos\theta_1} \cos\left(\frac{ga_1}{c^2} + \frac{1}{4}\pi\right), \tag{52}$$

$$\phi_2 = \frac{4\pi^{\frac{1}{2}}g^{\frac{1}{2}}\mathrm{H}\sec^3\theta_2}{c^3 a_2^{\frac{1}{2}}\sqrt{(\tan^2\theta_2 - \frac{1}{8})}}\, e^{-\frac{gf}{c^2}\sec^2\theta_2 - \mu\frac{a_2}{c}\cos\theta_2} \cos\left(\frac{ga_2}{c^2} - \frac{1}{4}\pi\right) \tag{53}$$

The calculation of the surface value of $\partial\phi/\partial z$ would follow the same course, but since the various expressions would merely contain an additional factor k, or κ as the case may be, under the integral signs, the results can be written down at once Thus

$$\frac{\partial\phi_1}{\partial z} = \frac{4\pi^{\frac{1}{2}}g^{\frac{3}{2}}\mathrm{H}\sec^5\theta_1}{c^5 a_1^{\frac{1}{2}}\sqrt{(\frac{1}{8} - \tan^2\theta_1)}}\, e^{-\frac{gf}{c^2}\sec^2\theta_1 - \mu\frac{a_1}{c}\cos\theta_1} \cos\left(\frac{ga_1}{c^2} + \frac{1}{4}\pi\right), \tag{54}$$

$$\frac{\partial\phi_2}{\partial z} = \frac{4\pi^{\frac{1}{2}}g^{\frac{3}{2}}\mathrm{H}\sec^5\theta_2}{c^5 q_2^{\frac{1}{2}}\sqrt{(\tan^2\theta_2 - \frac{1}{8})}}\, e^{-\frac{gf}{c^2}\sec^2\theta_2 - \mu\frac{a_2}{c}\cos\theta_2} \cos\left(\frac{ga_2}{c^2} - \frac{1}{4}\pi\right) \tag{55}$$

5 Our initial assumption of a frictional force varying as the velocity implies a dissipation of energy at a rate equal to 2μ times the kinetic energy This must be equal to $\mathrm{R}c$, where R is the resistance experienced by the moving solid Hence,

$$\mathrm{R} = -\frac{\mu\rho}{c}\iint \phi\frac{\partial\phi}{\partial n}\,d\mathrm{S}, \tag{56}$$

where the integration is taken over the boundary of the fluid, *i e*, practically over that portion of the free surface for which $x > 0$ We may further ignore all terms in the integral which do not vanish when $\mu \to 0$ The formula thus reduces to

$$\mathrm{R} = \frac{\mu\rho}{c}\iint\left(\phi_1\frac{\partial\phi_1}{\partial z} + \phi_2\frac{\partial\phi_2}{\partial z}\right)dx\,dy, \tag{57}$$

taken over the free surface.

Now from (51) or from a simple geometric calculation we find

$$\delta x\,\delta y = \frac{\partial(x, y)}{\partial(a, \theta)}\,\delta a\,\delta\theta = 2\cos^4\theta\,|\tfrac{1}{2} - \tan^2\theta|\,a\,\delta a\,\delta\theta \tag{58}$$

Hence

$$R = \frac{16\pi\mu\rho g^4 H^2}{c^9}\left\{\iint \sec^4\theta_1\, e^{-\frac{2gf}{c^2}\sec^2\theta_1 - 2\mu a_1\cos\theta_1}\, da_1\, d\theta_1 + \iint \sec^4\theta_2\, e^{-\frac{2gf}{c^2}\sec^2\theta_2 - 2\mu a_2\cos\theta_2}\, da_2\, d\theta_2\right\} \tag{59}$$

The range of a_1 and a_2 is from 0 to ∞ As regards θ_1 and θ_2 we may confine our attention as has been said to the fourth quadrant of the plane xy and in the end double the result Since θ_1 ranges from 0 to $\tan^{-1}\frac{1}{\sqrt{2}}$ and θ_2 from $\tan^{-1}\frac{1}{\sqrt{2}}$ to $\frac{1}{2}\pi$ the result is found when we finally make $\mu \to 0$ to be

$$R = \frac{16\pi\rho g^4 H^2}{c^8}\, I \tag{60}$$

where

$$I = \int_0^{\frac{1}{2}\pi} \sec^5\theta\, e^{-\frac{2gf}{c^2}\sec^2\theta}\, d\theta \tag{61}$$

As Havelock has pointed out in relation to the particular case of the sphere this integral can be expressed in terms of the Bessel Function*

$$K_n(z) = \int_0^\infty e^{-z\cosh u}\cosh nu\, du \tag{62}$$

In fact putting $\sec\theta = \cosh\frac{1}{2}u$ and taking account of the recurrence formula

$$K_{n-1}(z) - K_{n+1}(z) = -\frac{2n}{z}K_n(z) \tag{63}$$

we find

$$I = \tfrac{1}{4}e^{-\alpha}\left\{K_0(\alpha) + \left(1 + \frac{1}{2\alpha}\right)K_1(\alpha)\right\} \tag{64}$$

where $\alpha = gf/c^2$ A graph of R as a function of c is also given by him It indicates a maximum in the neighbourhood of $c = \sqrt{(gf)}$

It remains only to insert the value of H appropriate to the particular form of the solid For the sphere we find putting in (23) $A = \frac{2}{3}\pi b^3$ $Q = \frac{4}{3}\pi b^3$ where b is the radius

$$R = Mg\left(\frac{gf}{c^2}\right)^3 3I \tag{65}$$

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* I follow the notation of Watson, Theory of Bessel Functions, where tables are also given

where M′ is the mass of fluid displaced by the sphere If $c = \sqrt{(gf)}$ we find $R = 0{\cdot}2733\,M'g$

For a prolate spheroid moving in the direction of its polar axis ($2l$) we find

$$H = \tfrac{1}{3}e^2l^3 - \left\{\frac{1}{1-e^2} - \frac{1}{2e}\log\frac{1+e}{1-e}\right\}, \tag{66}$$

where e is the excentricity of the meridian For the oblate form

$$H = \tfrac{1}{3}e^2b^3 - \left\{\frac{\sin^{-1}e}{e} - \sqrt{(1-e^2)}\right\}, \tag{67}$$

where b is the equatorial radius *

6 We have not been concerned with the surface elevation In calculating it we may put $\mu = 0$ at once, wherever this does not make the expressions indeterminate It results then from a comparison of (20) with (21) that the difference from the calculation of ϕ will consist in a factor ik/σ after the integral signs in (33) The results can therefore be written down at once We have

$$\zeta = \zeta_1 + \zeta_2, \tag{68}$$

where

$$\zeta_1 = -\frac{4\pi^{\frac{1}{2}}g^{\frac{1}{2}}H\sec^4\theta_1}{c^4a_1^{\frac{1}{2}}\sqrt{(\frac{1}{2}-\tan^2\theta_1)}}e^{-\frac{gf}{c^2}\sec^2\theta_1}\sin\left(\frac{ga_1}{c^2}+\tfrac{1}{4}\pi\right), \tag{69}$$

$$\zeta_2 = -\frac{4\pi^{\frac{1}{2}}g^{\frac{1}{2}}H\sec^4\theta_2}{c^4a_2^{\frac{1}{2}}\sqrt{(\tan^2\theta_2-\frac{1}{2})}}e^{-\frac{gf}{c^2}\sec^2\theta_2}\sin\left(\frac{ga_2}{c^2}-\tfrac{1}{4}\pi\right) \tag{70}$$

It is unnecessary to dwell on the interpretation, which would follow the same lines as in the case of a pressure point travelling over the surface, which has been discussed by Kelvin and other writers, but it is to be noted that the elevation is now finite at the origin where $\theta_1 = 0$, $\theta_2 = \frac{1}{2}\pi$ There remains, however, a mathematical infinity at the cusps of the isophasal lines, where $\tan\theta_1 = \tan\theta_2 = \frac{1}{\sqrt{2}}$, but the formula (58) shows that the integral of the surface-elevation over any finite area, however small, is still finite

7 It has been assumed so far that the solid is moving along one of its axes of permanent translation, and that the remaining axes are horizontal and vertical, respectively It is plain, however, since the inertia coefficient A does not appear in (11), that a tilt about the first-named axis would make no difference. The case is altered if the body has a yaw in the horizontal plane

Let A_0, B_0, C_0 be the principal inertia coefficients of translation, so that the formula (7) reduces to

$$2T = A_0u^2 + B_0v^2 + C_0w^2 \tag{71}$$

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* 'Hydrodynamics,' Arts. 105, 108, 114

We will suppose in the first place that the axis to which C_0 refers is vertical, whilst that of A_0 makes an angle ω with the direction of motion. The coefficients in (11) have then the values

$$A = A_0 \cos^2 \omega + B_0 \sin^2 \omega, \quad C' = (A_0 - B_0) \sin \omega \cos \omega, \quad B' = 0 \qquad (72)$$

We must now add to (22) a term

$$K \frac{\partial}{\partial y} \frac{1}{r}, \quad \text{where} \quad K = \frac{C'c}{4\pi} \qquad (73)$$

The only difference will be that, so far as this term is concerned, the factor $\cos \psi$ in (32) must be replaced by $\sin \psi$, with the final result that we must replace the factors $H \sec^3 \theta_1$, and $H \sec^3 \theta_2$ which appear in the values of ϕ_1 and ϕ_2 by

$$(H + K \tan \theta_1) \sec^3 \theta_1 \quad \text{and} \quad (H + K \tan \theta_2) \sec^3 \theta_2,$$

respectively Similarly in the values of $\partial\phi_1/\partial z$ and $\partial\phi_2/\partial z$ we must replace $H \sec^5 \theta_1$ and $H \sec^5 \theta_2$ by

$$(H + K \tan \theta_1) \sec^5 \theta_1 \quad \text{and} \quad (H + K \tan \theta_2) \sec^5 \theta_2$$

Allowing for the different signs of $\tan \theta$ in the first and fourth quadrants we now find

$$R = \frac{16\pi\rho g^4}{c^6} \int_0^{\frac{1}{2}\pi} (H^2 + K^2 \tan^2 \theta) \sec^5 \theta \, e^{-\frac{2gf}{c^2}\sec^2\theta} d\theta$$

$$= \frac{16\pi\rho g^4}{c^6} (IH^2 + JK^2) \qquad (74)$$

where I is defined by (61) and

$$J = \int_0^{\frac{1}{2}\pi} \tan^2 \theta \sec^5 \theta e^{-\frac{2gf}{c^2}\sec^2\theta} d\theta$$

$$= \frac{1}{16\alpha} e^{-\alpha} \left\{ K_0(\alpha) + \left(1 + \frac{2}{\alpha}\right) K_1(\alpha) \right\}, \qquad (75)$$

as may be proved by the same substitution as in (61)

The corresponding values of the surface-elevation are found by replacing H in (69) and (70) by $H + K \tan \theta_1$ and $H + K \tan \theta_2$, respectively. The wave-pattern is now no longer symmetrical with respect to the direction of motion If the angle ω in (72) lies between 0 and $\frac{1}{2}\pi$, and $A_0 > B_0$, the waves will be higher in the quadrant where $\tan \theta_1$ and $\tan \theta_2$ are positive, i.e., on the side towards which the yaw is The reverse will be the case if $A_0 < B_0$

If the solid has a tilt β in the vertical plane of motion, the inertia coefficients are

$$A = A_0 \cos^2 \beta + C_0 \sin^2 \beta, \quad C' = 0, \quad B' = (A_0 - C_0) \sin \beta \cos \beta \qquad (76)$$

We must now add to (22) a term

$$B'c \frac{\partial}{\partial z} \frac{1}{r} = - B'c \int_0^\infty e^{-k(f+z)} J_0 (k\bar{\omega})\, k\, dk \qquad (77)$$

Compensating this so as to make $\phi = 0$ at the surface, as in (27), we find that the addition to the initial surface value of $\partial\zeta/\partial t$ in (28) is, in the present case, zero The wave resistance, and surface-elevation, are therefore given by the same formula as in the case of symmetry, provided we substitute the value of A from (76)

On the Electrostatic Potential Energy, and the Rhombohedral Angle, of Carbonate and Nitrate Crystals of the Calcite Type

By S Chapman, F R S, J Topping, M Sc, and J Morrall, M Sc

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§ 1 *Introduction*

§ 1.1 This paper is a sequel to, and an extension of, one with a somewhat similar title by W L Bragg and S Chapman,[*] in which it was shown that, on certain natural assumptions, the rhombohedral angle could be calculated for the well-known isomorphous series of carbonate crystals of the calcite type The detailed results and the method of calculation were not described This is done in the present paper, where also the results of a parallel calculation for a similar possible series of nitrate crystals is given, the only known nitrate crystal of this type, however, is that of sodium, the corresponding potassium salt crystallising in the aragonite form[†]

§ 1 2 As the underlying principles of the method have been described in the paper cited, they need only receive brief mention here The crystals considered are supposed to consist of positive and negative ions, namely, metallic ions

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[*] 'Roy. Soc Proc,' A, vol 106, p 346 (1924)

[†] W L. Bragg 'Roy Soc. Proc,' A, vol 105, pp 16 and 370 (1924).

(doubly charged, like Ca^{++} in the carbonate series, or singly charged like Na^{+} in the nitrate case), and ionised groups CO_3^{--} (i.e., C^{++}_{++}, O^{--}, O^{--}, O^{--}) or NO_3^{-} (i.e. N^{+++}_{++}, O^{--}, O^{--}, O^{--}). The detailed arrangement of these groups is described in § 2.4, but if the CO_3 or NO_3 groups are treated as wholes, the arrangement of the positive and negative ions is similar to that of the ions in a simple cubic crystal of the rock salt type, except that the cubic lattice is contracted—into a rhombohedral lattice parallel to one diagonal; this diagonal thus becomes the trigonal axis of the crystal. The edges meeting in the trigonal axis are inclined to one another at an angle (the "rhombohedral angle") of about 102°, instead of 90° in the case of rock-salt.

§ 1.3. The equilibrium of the crystal is supposed to be maintained by the joint action of electrostatic forces (attractions and repulsions) between the various ions, together with certain other repulsive forces such as those which come into play at close approximations (collisions) of molecules in gases. These will be referred to as *the* repulsive forces; they are known to vary much more rapidly with distance between the ionic centres than do the electrostatic forces, namely, by the ninth or some higher power of the inverse distance in the former case, as against the second in the latter case. The repulsive forces between other than immediately adjacent ions are therefore probably negligible, and it will be assumed here that this is so; each O ion is in contact with two equidistant Ca^{++} (or two Na^{++}) ions, and each Ca^{++} (or Na^{++}) ion is in contact with six equidistant O^{--} ions. (*Cf.* § 13.5, where the relative distances of the next nearest (non adjacent) pairs of ions are all given.)

§ 1.4. In a state of stable equilibrium the whole set of ions will adopt a grouping which renders the total potential energy a minimum. The change of potential energy corresponding to any small first-order change in the ionic grouping will therefore be zero (that is, of the second order). If a displacement is considered in which the form and size of the CO_3 (or NO_3) ionic groups remain unaltered, and in which also the distance between neighbouring pairs of O and Ca (or O and Na) ions is preserved, there will be no change in the potential energy of the repulsive forces, in so far as the above assumption (§ 1.3) is correct; the whole change will be in the electrostatic potential energy. The size of the CO_3 (and NO_3) groups, and the distance between neighbouring O and Ca (or Na) ions are known from X-ray measurements (but *cf.* § 13), they do not suffice to determine the rhombohedral angle α. This, therefore, may be treated as a variable parameter, and if the electrostatic potential energy corresponding to several values of α is calculated, the value of α which makes that energy a minimum should correspond to the equilibrium or actual value of α. As described in the former paper, the results on the whole confirm this expectation, though their interpretation is not without ambiguity, owing to some uncertainty as to the exact position of the force-centres within the ions The questions involved here are discussed in § 13 of this paper

§ 1 5 Since carbonates of different metals are under discussion, the distance between the centres of immediately adjacent O and metallic ions will vary from one salt to another * Thus the geometry of the ionic lattice will be taken to involve two variable ratios or parameters, which correspond to the rhombohedral angle α and to the ratio of the distance between an O ion and an adjacent metallic ion, to the distance between an O ion and the neighbouring C ion In the actual calculation it is found convenient to replace these by two alternative parameters *t* and λ (*cf* §§ 4 3 and 2 3)

§ 1 6 The calculation therefore relates to the electrostatic potential energy (per unit volume or unit cell) of an infinite lattice of point charges involving two parameters *t*, λ The results can be indicated graphically by contour or equipotential lines on a diagram in which *t* and λ are ordinates, these lines being drawn so as to pass through points (or pairs of values of λ and *t*) for which the electrostatic potential energy has a constant value On the same diagram lines (called configuration curves) can be drawn which indicate the relation between λ and *t*, as α is varied, as above described, for a crystal in which the size of the CO_3 ion and the distance between an O ion and the metallic ion are fixed The equipotential lines indicate how the energy varies in such a change of configuration, where the configuration curve touches an equipotential line, a state of maximum or minimum potential energy is indicated This will correspond to an equilibrium configuration of the given crystal

In the present paper two such diagrams are drawn (figs 3 and 4), one for carbonate crystals and one for nitrate crystals (*cf* § 12 1) Fig 3 covers a wider range of the parameters than does the corresponding figure on p 374 of the former paper cited above

When combined with the corresponding values of the potential energy arising from the repulsive forces, the present calculations have wider applications than are made in this paper Some of these it is hoped to discuss in a later paper in collaboration with Dr J E Lennard-Jones

Subsequent to the former paper by W L Bragg and S Chapman, a theoretical calculation of the form of a simpler series of crystals (rutile and anatase), involving one parameter only instead of two, has been made by M Born and

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* The size of the CO_3 ionic group is supposed to be the same in all the members of the calcite series of crystals; this group is so tightly bound together by electrostatic forces that variations in the metallic ion are unlikely to affect the CO_3 group appreciably

O Bollnow,[*] using a method given by Eward [†] The results appear to be in satisfactory accord with observation

The authors wish to acknowledge the advantage they have derived from consultations with Prof W L Bragg on some of the physical questions involved in this paper

THE ELECTROSTATIC POTENTIAL ENERGY OF A CALCITE LATTICE OF POINT CHARGES

§ 2 *Geometrical Description and Analysis of the Lattice*

§ 2 1 The point charges of the lattice to be considered lie in planes, spaced at constant distance d apart, perpendicular to the trigonal axis of the crystal Let $\mathbf{d}$ denote a vector of magnitude d, having the direction of the trigonal axis Then, starting from a given plane, numbered zero, the successive planes will be numbered s ($s = \pm 1, \pm 2$), corresponding to a displacement $s\mathbf{d}$ from the given plane

In each plane there lie either only CO_3 groups of charges, or only Ca charges,[‡] and planes of the two kinds occur alternately Choosing a CO_3 plane for the plane $s = 0$, all the planes for which s is even will be CO_3 planes, while those for which s is odd will be Ca planes

§ 2 2 In any plane the C or Ca ions are situated at the corners of an equi-triangular network, these networks are of the same dimensions and similarly orientated in all the planes The sides of any such elementary triangle, taken in order round the triangle, may be represented in direction and magnitude by three vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, of equal length a

These vectors will clearly satisfy the equation

$$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 = 0,$$

so that the third can be expressed in terms of the first two Taking any point of such a network as origin, the position of any other point of the network can be specified by its displacement vector from the origin, in the form

$$m\,\mathbf{a}_1 + n\,\mathbf{a}_2,$$

where m and n are any positive or negative integers this expression suffices, without ambiguity, to represent all points of the network

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[*] Born and Bollnow, "Zur Gittertheorie des Rutils" in 'Naturw,' vol 13, p 559 (1925); and "Zur Gittertheorie des Anatas" in 'Nachr d Ges d Wiss zu Göttingen' (1925)

[†] Born, 'Atomtheorie des Festen Zustandes," 2nd Aufl., p 727 (1925)

[‡] The metallic ions will be referred to, for definiteness, as Ca ions; but they will simply signify double positive charges, and may be ions of any other metal forming carbonate crystals isomorphous with calcite

§ 2.3 In successive planes these networks are not immediately above or below each other, when viewed parallel to the trigonal axis There is a displacement of the network in plane $s+1$, relative to that in plane s, of amount $\frac{1}{3}(\mathbf{a}_1-\mathbf{a}_3)$, consequently, the net-points in plane $s+1$ lie over the centres of alternate triangles of the network in plane s the further displacement of the network in plane $s+2$ makes the net-points in this plane lie over the centres of the remaining triangles in plane s The still further displacement of the network in plane $s+3$ (the total shift relative to plane s being $\mathbf{a}_1-\mathbf{a}_3$) makes the net-points in this plane lie over those in plane s If the plane s is a CO_3 plane, the plane $s+3$ will be a Ca plane, and vice versa not till plane $s+6$ is reached are both the disposition and the kind of charges at the net-points the same as in plane s

In any CO_3 plane the three O ions of any CO_3 group lie at equal distances λa (where λ is a positive fraction) from their central C ion along three alternate members of the set of six radii of the network through this ion, that is, relative to this C ion their positions are given either by $\lambda\mathbf{a}_1$, $\lambda\mathbf{a}_2$, $\lambda\mathbf{a}_3$ or by $\lambda\mathbf{a}_1$, $-\lambda\mathbf{a}_2$, $-\lambda\mathbf{a}_3$. In each CO_3 plane the arrangement is the same for all the CO_3 ionic groups, and the two arrangements occur alternately in successive CO_3 planes Hence the CO_3 groups in planes s and $s+6$ (s being even) differ in the arrangement of the O ions around the C ions, not till plane $s+12$ is reached does the arrangement in plane s recur completely

§ 2 4 The positions of the whole set of charges in the lattice (which for brevity will be termed the lattice L) may be concisely specified as follows, relative to a C ion in the CO_3 plane $s=0$ For definiteness the O ions in this plane will be supposed to be displaced from the C ion of the same CO_3 group by the amounts $-\lambda(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ Let l, m, n denote any positive or negative integers, and e the (positive) electronic charge

Let

$$\mathbf{r}_{s,m,n} \equiv s\mathbf{d} + m\mathbf{a}_1 + n\mathbf{a}_2, \tag{1A}$$

$$\mathbf{r}'_{s,m,n} \equiv \mathbf{r}_{s,m,n} + \tfrac{1}{3}(\mathbf{a}_1-\mathbf{a}_3), \tag{1B}$$

$$\mathbf{r}''_{s,m,n} \equiv \mathbf{r}_{s,m,n} + \tfrac{2}{3}(\mathbf{a}_1-\mathbf{a}_3) \tag{1C}$$

Then the planes for which s is even are CO_3 planes, in which the C ions are at points $\mathbf{r}_{s,m,n}$, $\mathbf{r}'_{s,m,n}$, or $\mathbf{r}''_{s,m,n}$, as follows, while the O ions are displaced by either $+\lambda$ or $-\lambda$ times $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ from the C ion of their CO_3 group, as indicated below, for convenience in printing, the suffixes s, m, n to $\mathbf{r}$, $\mathbf{r}'$, $\mathbf{r}''$ are omitted

CO_3 plane s	$12l$	$12l+2$	$12l+4$	$12l+6$	$12l+8$	$12l+10$
Positions of C ions	$\mathbf{r}$	$\mathbf{r}''$	$\mathbf{r}'$	$\mathbf{r}$	$\mathbf{r}''$	$\mathbf{r}'$
Sign of λ	$-$	$+$	$-$	$+$	$-$	$+$

For example, in the plane $s = 12l$, there are charges $4e$ (C ions) at the points $\mathbf{r}_{l,m,n}$ and charges $-2e$ (O ions) at the three sets of points $\mathbf{r} - \lambda\mathbf{a}_1$, $\mathbf{r} - \lambda\mathbf{a}_2$, $\mathbf{r} - \lambda\mathbf{a}_3$

The planes for which s is odd are Ca planes, and there are charges $2e$ (Ca ions) at the points $\mathbf{r}$, $\mathbf{r}'$ $\mathbf{r}''$ as follows

s	$12l+1$	$12l+3$	$12l+5$	$12l+7$	$12l+9$	$12l+11$
Positions of Ca ions	$\mathbf{r}'$	$\mathbf{r}$	$\mathbf{r}''$	$\mathbf{r}'$	$\mathbf{r}$	$\mathbf{r}''$

In this specification the implied suffixes l, m, n take all the values obtained by letting l, m n have any zero positive or negative integral values

§ 2 5 This whole lattice of points specified relative to a given C ion, and excluding this ion, will be termed the lattice L_C If we change the origin to a neighbouring Ca ion say, in the plane $s = 1$, we must subtract $\mathbf{d} + \frac{1}{3}(\mathbf{a}_1 - \mathbf{a}_3)$ from all the above position vectors The corresponding lattice of points, excluding the Ca ion at the origin, will be termed the lattice L_{Ca} Similarly, if we change the origin to any one of the three O ions at $-\lambda\mathbf{a}_1$, $-\lambda\mathbf{a}_2$ or $-\lambda\mathbf{a}_3$ the corresponding lattices, excluding the O ion chosen as origin, will be termed the lattices L_1 L_2, L_3

Fig 1 shows the positions of the points $\mathbf{r}$, $\mathbf{r}'$ $\mathbf{r}''$ represented by dots, circles and crosses projected on the plane $s = 0$ The vectors $\mathbf{a}_1$ $\mathbf{a}_2$, $\mathbf{a}_3$ are also indicated

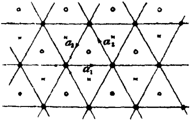

Fig 1

§ 2 6 Each O ion may be regarded as in "contact" with two Ca ions, which are those immediately adjacent to it For example, the O ion at $-\lambda\mathbf{a}_1$ (relative to a C ion in the plane $s = 0$) is in contact with two equidistant Ca ions at the points $\mathbf{d} + \frac{1}{3}(\mathbf{a}_2 - \mathbf{a}_1)$ and $-\mathbf{d} + \frac{1}{3}(\mathbf{a}_3 - \mathbf{a}_1)$

Each Ca ion is in contact with six equidistant O ions taking any such Ca ion as origin, the relative position vectors of the six O ions are

$$-\mathbf{d} + \tfrac{1}{3}(\mathbf{a}_2 - \mathbf{a}_3) - \lambda\mathbf{a}_2, \quad -\mathbf{d} + \tfrac{1}{3}(\mathbf{a}_3 - \mathbf{a}_1) - \lambda\mathbf{a}_3, \quad -\mathbf{d} + \tfrac{1}{3}(\mathbf{a}_1 - \mathbf{a}_2) - \lambda\mathbf{a}_1$$

together with these same vectors reversed

The distance f between a pair of adjacent O and Ca ions is given by the equation :

$$f^2 = (-\mathbf{d} + \tfrac{1}{3}\mathbf{a}_2 - \tfrac{1}{3}\mathbf{a}_3 - \lambda\mathbf{a}_2,\ -\mathbf{d} + \tfrac{1}{3}\mathbf{a}_2 - \tfrac{1}{3}\mathbf{a}_3 - \lambda\mathbf{a}_2)$$

in which the right-hand side is simply the square of the first of the position vectors just indicated

Since $(\mathbf{d}, \mathbf{a}_2) = 0$, $(\mathbf{d}, \mathbf{a}_3) = 0$, $(\mathbf{a}_2, \mathbf{a}_3) = -\tfrac{1}{2}a^2$ we have

$$\begin{aligned} f^2 &= d^2 + (\lambda - \tfrac{1}{3})^2 a^2 + \tfrac{1}{3}a^2 - 2(\lambda - \tfrac{1}{3})\ \tfrac{1}{3}\ \tfrac{1}{2}a^2, \\ &= d^2 + (\lambda^2 - \lambda + \tfrac{1}{3})a^2 \end{aligned} \tag{2}$$

§ 3 *The Electrostatic Potential Energy of the Lattice*

§ 3 1 The crystal lattice is supposed to extend to infinity in every direction The total electrostatic potential energy of the crystal is $\frac{1}{2}\Sigma EV$, where E refers to any one of the point charges, and V to the electrostatic potential at that point due to all the remaining charges the summation is to be extended over all the charges The sum will, of course, be infinite , what we wish to know is the value of the sum (W, say) extended over the five ions of one $CaCO_3$ molecule, viz

$$W = \tfrac{1}{2}\{4eV_C - 3 \cdot 2eV_O + 2eV_{Ca}\},$$

where V_C, V_O, V_{Ca} denote the value of V at the corresponding ions , owing to the symmetry of the structure, V has the same value at all ions of the same kind

Writing the last equation in the form

$$W = \tfrac{1}{2}e\{4V_C - 3 \cdot 2V_O + 2V_{Ca}\}, \tag{3}$$

$W/\frac{1}{2}e$ may be interpreted as the potential at a point P due to a composite lattice (L_P) of charges, constituted of a lattice whose arrangement relative to P is the same as that of the lattice L_C (§ 2 5) relative to a C ion, but with all the charges quadrupled , a lattice geometrically the same as L_{Ca} (§ 2 5), but with all the charges doubled , and three lattices of type L_1, L_2 L_3 (§ 2 5) but with all the charges doubled and reversed

§ 3.2 It may readily be verified that the charges of the lattice L_P are arranged as follows in successive planes s, reckoning $s = 0$ as the plane through P normal to the trigonal axis The charges in each plane will form groups arranged at and around the points of the same equitriangular networks as are specified (relative to a C ion) in § 2 4 The charges at and around each such point can be described as a charge $\pm 8e$ at the lattice-point, together with a group of charges in which the total charge is zero Four kinds of these groups occur, which will be denoted by the letters G_1, G_2, G_3, G_4, they are illustrated in fig 2, the centre of each group being supposed situated at

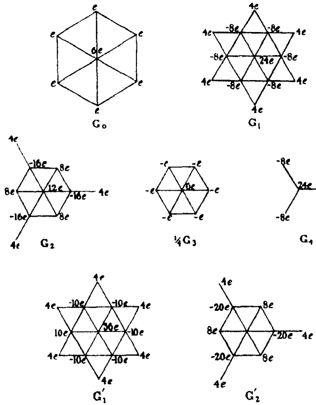

FIG 2

a lattice-point The arrangement of the lattice-point charges and the groups around them, in the various planes, is as shown in Table I

§ 3 3 To determine W (§ 3 1) we have to calculate the potential of this composite lattice of charges L_P, at P This has been done by re-dividing the lattice into (α), the charges $\pm 8e$ at the lattice-points in all the planes (but excluding the origin, *cf* § 2 5), (β) the sets of neutral groups in all the planes $s \neq 0$, and (γ) the sets of neutral groups in the plane $s = 0$ The potentials corresponding to these parts of L_P will be denoted by V_α, V_β, V_γ, respectively, and will be considered in this order

Table I

Value of s	Positions of Lattice Points	Charge at Lattice Points	Neutral Groups around Lattice Points
$12l$	$\mathbf{r}$	$8e$	G_1
$12l+1$	$\mathbf{r}$	$-8e$	G_4
$12l+2$	$\mathbf{r}''$	$8e$	G_2
$12l+3$	$\mathbf{r}$	$-8e$	G_3
$12l+4$	$\mathbf{r}$	$8e$	G_1
$12l+5$	$\mathbf{r}''$	$-8e$	G_4
$12l+6$	$\mathbf{r}$	$8e$	G_2
$12l+7$	$\mathbf{r}$	$-8e$	G_3
$12l+8$	$\mathbf{r}''$	$8e$	G_1
$12l+9$	$\mathbf{r}$	$8e$	G_4
$12l+10$	$\mathbf{r}$	$8e$	G_2
$12l+11$	$\mathbf{r}''$	$-8e$	G_3

§ 4 *The Potential of the Charges ± 8e at the Lattice Points*

§ 4 1 The first part of the potential to be considered is that due to the charges $\pm 8e$ at the lattice points whose positions are given in Table I (§ 3 2). These points may be divided into three groups according as their position vectors are expressed by $\mathbf{r}$ (for $s - 12\,l = 0, 3, 6, 9$), $\mathbf{r}$ (for $s - 12\,l = 1, 4, 7, 10$), or $\mathbf{r}''$ (for $s - 12\,l = 2, 5, 8, 11$), in any one such group the points may be divided into linear series in each of which m, n remain constant and s varies The distance between consecutive points in each linear series is $3\,d$, and positive and negative charges alternate along each series, such a series is therefore electrically neutral as a whole

§ 4 2 The potential at a point P due to such a linear series of charges $\pm 8e$, alternately positive and negative and arranged at equal distances $3d$, is deducible from a formula given by Madelung * and is

$$V = \frac{64e}{6d} \sum_{\substack{l=1 \\ (\text{odd})}}^{\infty} K_0\left(\frac{2\pi l\rho}{6d}\right) \cos \frac{2\pi l x}{6d} \tag{4}$$

In this formula ρ denotes the magnitude of the vector $\boldsymbol{\rho} = \mathrm{PN}$, where N is the foot of the perpendicular from P on to the line, and x denotes the distance of N from the nearest positive charge along the line

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* Madelung, 'Phys Zeit,' vol 19, p 524 (1918) The function K_0 is a Bessel function of imaginary argument *Cf* G N Watson, 'Theory of Bessel Functions,' p 78 (Cambridge, 1922) Values of $K_0(u)$ to 20 decimal places have been given by Aldis ('Roy Soc. Proc,' A, vol 64) for a range of u from 0 to 12 at intervals of 0 1. For the present work it was found convenient to construct a table, using the ordinary interpolation formulæ, giving values of $K_0(u)$ over the same range of u, but at intervals of 0 001

In the present case the potential is required at the origin so that in the above three groups of charges $\boldsymbol{\rho}$ and x have the following values —

$$\begin{array}{lll} \text{Group } \mathbf{r} & \boldsymbol{\rho} = m\mathbf{a}_1 + n\mathbf{a}_2 & x = 0 \\ \text{Group } \mathbf{r}' & \boldsymbol{\rho} = m\mathbf{a}_1 + n\mathbf{a} + \tfrac{1}{3}(\mathbf{a}_1 - \mathbf{a}_2) & x = d \\ \text{Group } \mathbf{r}'' & \boldsymbol{\rho} = m\mathbf{a}_1 + n\mathbf{a}_2 + \tfrac{2}{3}(\mathbf{a}_1 - \mathbf{a}_2) & x = 2d \end{array}$$

The calculation of the potential at the origin due to the series $m = n = 0$ in the group $\mathbf{r}$ (in which case $\boldsymbol{\rho} = 0$) cannot be made by the above formula the potential of this series is clearly —

$$\begin{aligned} \mathrm{V} &= 2\left(-\frac{8e}{3d} + \frac{8e}{6d} - \frac{8e}{9d} + \quad\right) \\ &= -16e/3d \ \log_e 2 \end{aligned}$$

the factor 2 being included to account for the charges on both sides of the origin

§ 4 3 The total potential is given by summing the above series (in equation (4)) for all the values of $\boldsymbol{\rho}$ in the three groups obtained when m and n take all positive and negative integral values (really infinite in number) But for the present purpose it is unnecessary to consider values of l and $\boldsymbol{\rho}$ that is values of l m and n which make the argument of K $(2\pi l\rho/6d)$ greater than 12

Thus the total expression for the potential of these charges becomes

$$\begin{aligned} \mathrm{V}_s = -\frac{16e}{3d}\log_e 2 + \frac{64e}{d}\Big[&-\{\tfrac{1}{2}\mathrm{K}_0(t) + \tfrac{1}{2}\mathrm{K}_0(2t) + \mathrm{K}_0(t\sqrt{7}) + \mathrm{K}_0(t\sqrt{13}) \\ &\quad + \tfrac{1}{2}\mathrm{K}_0(4t) + \mathrm{K}_0(t\sqrt{19}) + \mathrm{K}_0(5t) \\ &\quad + \mathrm{K}_0(2t\sqrt{7}) + \mathrm{K}_0(t\sqrt{31}) + \mathrm{K}_0(t\sqrt{37}) \\ &\quad + \mathrm{K}_0(t\sqrt{43}) + \mathrm{K}_0(2t\sqrt{13}) + \mathrm{K}_0(t\sqrt{61}) \\ &\quad + \mathrm{K}_0(t\sqrt{67}) + \tfrac{1}{2}\mathrm{K}_0(8t) + \mathrm{K}_0(t\sqrt{73}) \\ &\quad + 2\mathrm{K}_0(7t)\} \\ &+ \mathrm{K}_0(t\sqrt{3}) + 2\mathrm{K}_0(3t) + \mathrm{K}_0(2t\sqrt{3}) + 2\mathrm{K}_0(t\sqrt{21}) \\ &+ 2\mathrm{K}_0(3t\sqrt{3}) + 2\mathrm{K}_0(6t) + 2\mathrm{K}_0(t\sqrt{39}) \\ &+ \mathrm{K}_0(4t\sqrt{3}) + 2\mathrm{K}_0(t\sqrt{57}) + 4\mathrm{K}_0(3t\sqrt{7})\Big] \qquad (5) \end{aligned}$$

where for convenience the parameter $t = \pi a/3d\sqrt{3}$ is introduced (*cf* § 1 5)

Equation (5) may be written

$$\mathrm{V}_s = -(64e/6d)\left[\tfrac{1}{2}\log_e 2 - 6f(t)\right]$$

where $f(t)$ is the sum of the K_0 functions—the expression in square brackets in equation (5) The factor $64e/6d$ may be written $(192e/b)\ \lambda t/2\pi\sqrt{3}$, and consequently we can write equation (5) in the form

$$V_s = -\,(192e/b)\ \phi_s(\lambda, t), \tag{6}$$

where

$$\phi_s(\lambda, t) = (\lambda t/2\pi\sqrt{3})\,[\tfrac{1}{2}\log_e 2 - 6f(t)] \quad \text{and} \quad b = \lambda a$$

The distance b defines the size of the CO_3 ionic group, and is the constant distance from the C ion to the O ions of the same group

Values of $\phi_s(\lambda, t)$ were calculated for a series of values of λ at intervals of 0 05 from 0 to 0 25, and for values of t at intervals of 0 2 from 1 4 to 3 2. The values of $\phi_s(\lambda\ t)$ are given in Table II

Table II —Values of $\phi_s(\lambda, t)$

t	$\lambda = 0$	0 05	0 10	0 15	0 20	0 25
1 4	0	0 005 045	0 010 090	0 015 135	0 020 181	0 025 226
1 6	0	5 269	10 538	15 808	21 077	26 346
1 8	0	5 412	10 824	16 236	21 648	27 060
2 0	0	5 514	11 028	16 542	22 056	27 570
2 2	0	5 600	11 200	16 801	22 401	28 001
2 4	0	5 687	11 373	17 060	22 746	28 433
2 6	0	5 782	11 565	17 347	23 130	28 912
2 8	0	5 894	11 787	17 681	23 575	29 468
3 0	0	6 023	12 046	18 068	24 091	30 114
3 2	0	6 171	12 342	18 513	24 684	30 855

§ 5 *The Potential of the Neutral Groups in the Planes $s \neq o$*

§ 5 1 To obtain an expression for the potential of the sets of neutral groups in the other planes, we make use of a formula proved by Madelung* (using rectangular co-ordinates) for the potential of a plane network of charges The network considered consists of two parallel line series of charges so arranged that the charges lie at the corners of parallelograms with sides a, b and angle ϕ In the special case $a = b$ and $\phi = 60°$, it can be shown that, in terms of oblique co-ordinates (x, y) along the sides of the parallelograms, Madelung's formula reduces to ·

$$V = \frac{E}{a}\sum_{-\infty}^{\infty}{}'\sum \frac{e^{\frac{-4\pi z}{a\sqrt{3}}(l^2+lm+m^2)^{\frac{1}{2}}}}{(l^2+lm+m^2)^{\frac{1}{2}}}\cos\frac{2\pi}{a}(lx - my) - \frac{4\pi E}{a^2\sqrt{3}}\ z + K_2, \tag{7}$$

where E is the charge at each point of the network, z denotes distance measured perpendicular to the network and K_2 is a constant The accent (′)

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* Madelung, *loc cit*

in the summation sign indicates that although l and m may be zero, they do not take simultaneous zero values

This formula can be applied to find the potential of a network at each point of which there is a G_1, G_2, G_3 or G_4 group of charges

§ 5 2 *Potential of a Network of* G_3 *or* G_4 *Groups*—Consider new co ordinates (ξ, η) such that

$$2\pi x/a = \xi \text{ and } 2\pi y/a = \eta \quad \text{Also write } \beta = 2\pi\lambda$$

Then a G_4 group of charges consists of a charge $24e$ at a point, together with charges $-8e$ at the points (β, o), $(o, -\beta)$ and $(-\beta, \beta)$ relative to this Hence the potential of a network of G_4 groups is given by the formula (7) in which $E = 24e$, less three similar expressions in which $E = 8e$ and (i) ξ is replaced by $\xi - \beta$, (ii) η by $\eta + \beta$, and (iii) ξ, η by $\xi + \beta, \eta - \beta$ respectively

Thus in the resultant expression for V the last two terms in (7) disappear the first factor in the summed terms remains as above (since all members of the G_4 groups in a plane have the same z), and the trigonometrical factor in (7) becomes —

$$24 \cos(l\xi - m\eta) - 8 \cos(l\xi - m\eta - l\beta)$$
$$- 8 \cos(l\xi - m\eta - m\beta) - 8 \cos(l\xi - m\eta + l\beta + m\beta),$$

which readily reduces to

$$8 \cos(l\xi - m\eta)\{2 \sin^2 \tfrac{1}{2}l\beta + 2 \sin^2 \tfrac{1}{2}m\beta + 2 \sin^2 \tfrac{1}{2}(l + m)\beta\}$$
$$- 32 \sin(l\xi - m\eta) \sin \tfrac{1}{2} l\beta \sin \tfrac{1}{2} m\beta \sin \tfrac{1}{2}(l + m)\beta \qquad (8)$$

In the present paper the only relevant values of (ξ, η) are

(*a*) $\xi = \eta = 0$, in which case the second term in (8) vanishes for every combination of l and m.

(*b*) $\xi = \eta = \tfrac{2}{3}\pi$, for which the sum of the values of the second term in (8) for all values of l and m is zero, since the values of this term for combinations of l and m such as (2 3) and (3 2) cancel, and $\sin(l\xi - m\eta)$ vanishes when $l = m$

Hence the potential of a network of G_4 groups is —

$$V = 8e/a \sum_{-\infty}^{\infty}{}' \sum \exp(\delta_0 z) \;\phi(l, m) \;\cos(l\xi = m\eta), \qquad (9)$$

where

$$\phi(l, m) = 2\,[\sin^2 \tfrac{1}{2}l\beta + \sin^2 \tfrac{1}{2}m\beta + \sin^2 \tfrac{1}{2}(l + m)\beta]/(l^2 + lm + m^2)^{\frac{1}{2}},$$

and

$$\delta_0 = -(4\pi/a\sqrt{3}) \;(l^2 + lm + m^2)^{\frac{1}{2}}$$

Since a reversal of the sign of β leaves $\phi(l, m)$ unaltered, it is clear that the potential of a network of G_3 groups is the same as that of a network of G_4 groups

§ 5 3 *Potential of a Network of* G_1 *Groups* —A G_1 group of charges consists of a $2G_3$ group together with the following additional charges $-24e$ at the centre of the group and charges $4e$ at points (β, β), $(-\beta, -\beta)$, $(2\beta, -\beta)$, $(-2\beta, \beta)$, $(-\beta, 2\beta)$ and $(\beta, -2\beta)$ relative to the centre The potential of a network, about each point of which there is a group of these additional charges, is obtained by taking the original formula (7) and substituting $E = -24e$, together with six similar expressions in which (i) $E = 4e$ and (ii) ξ, η is suitably altered in each case, as in arriving at the expression (8)

It is clear that the resultant formula will involve

$$\begin{aligned}-24\cos(l\xi - m\eta) &+ 4\cos(l\xi - m\eta + \overline{l-m}\beta) + 4\cos(l\xi - m\eta + \overline{l+2m}\beta)\\ &+ 4\cos(l\xi - m\eta + \overline{2l+m}\beta) + 4\cos(l\xi - m\eta - \overline{l-m}\beta)\\ &+ 4\cos(l\xi - m\eta - \overline{l+2m}\beta) + 4\cos(l\xi - m\eta - \overline{2l+m}\beta),\end{aligned}$$

which reduces to

$$-8\cos(l\xi - m\eta)\{2\sin^2\tfrac{1}{2}(l+2m)\beta + 2\sin^2\tfrac{1}{2}(2l+m)\beta + 2\sin^2\tfrac{1}{2}(l-m)\beta\}$$

Hence the potential of a network of G_1 groups is

$$V = (8e/a)\sum_{-\infty}^{\infty}{}'\sum \exp\ (\delta_0 z)\ \{2\phi(l, m) - \psi(l, m)\}\ \cos(l\xi - m\eta), \qquad (10)$$

where

$$\psi(l, m) = 2\{\sin^2\tfrac{1}{2}(l+2m)\beta + \sin^2\tfrac{1}{2}(2l+m)\beta + \sin^2\tfrac{1}{2}(l-m)\beta\}/(l^2+lm+m^2)^{\frac{1}{2}}$$

§ 5 4 *Potential of a Network of* G_2 *Groups* —It is clear from fig 2 that a G_2 group of charges consists of a G_4 group, together with a G_4 group in which (i) the charges have been reversed in sign and halved, and (ii) the displacements of the charges doubled

Hence the potential of a network of G_2 groups is

$$V = 8e/a\ \sum_{-\infty}^{\infty}{}'\sum \exp\ (\delta_0 z)\ \{\phi(l, m) - \tfrac{1}{2}\phi(2l, 2m)\}\ \cos(l\xi - m\eta) \qquad (11)$$

§ 5 5 The formulæ (9), (10), (11) give the potential at the origin due to a plane network of either G_3, G_4, G_1 or G_2 groups of charges in a plane at a distance z from the origin, and displaced relatively to the origin as indicated by (ξ, η)

It is now necessary to combine these formulæ so as to obtain the complete potential for all such planes, the distribution of which is indicated in Table I. It is convenient to write

$$\delta = \delta_0 d \equiv -(4\pi^2/9t)\ \ (l^2 + lm + m^2)^{\frac{1}{2}} \quad (Cf\ \S\,5\,1\,)$$

$$X = \phi(l, m)\,, \quad Y = 2\phi(l, m) - \psi(l, m) \quad \text{and} \quad Z = \phi(l, m) - \tfrac{1}{2}\phi(2l, 2m)$$

Hence in this notation we have, for the potential of the G_3 and G_4 groups on both sides of the central plane $s = 0$ —

$$2\,(8e/a)\,\sum_{-\infty}^{\infty}{}'\sum X\,[\{\exp\ \delta + \exp\ 5\delta + \exp\ 7\delta + \ \ \}\cos \tfrac{1}{2}\pi\,(l - m)$$
$$+ \exp\ 3\delta + \exp.\ 9\delta + \ \ ],$$

for the potential of the G_1 groups on both sides of the central plane —

$$2\,(8e/a)\,\sum_{-\infty}^{\infty}{}'\sum Y\,[\{\exp\ 4\delta + \exp\ 8\delta + \exp\ 16\delta + \ \ \}\cos \tfrac{1}{2}\pi\,(l - m)$$
$$+ \exp\ 12\delta + \ \ ],$$

and for the potential of the G_2 groups on both sides of the central plane —

$$2\,(8e/a)\,\sum_{-\infty}^{\infty}{}'\sum Z\,[\{\exp\ 2\delta + \exp\ 10\delta + \exp\ 14\delta + \ \ \}\cos \tfrac{1}{2}\pi\,(l - m)$$
$$+ \exp\ 6\delta + \ \ ]$$

In the subsequent numerical calculations the exponential terms beyond exp 8δ may be neglected Omitting these, the potential of the whole set of neutral groups outside the plane $z = 0$, is given by —

$$\begin{aligned} V_s = (16e/a)\sum_{-\infty}^{\infty}{}'\sum\,[&X\,(\exp\ \delta + \exp\ 5\delta + \exp\ 7\delta)\cos \tfrac{1}{2}\pi\,(l - m) + X \exp\ 3\delta \\ &+ Y\,(\exp\ 4\delta + \exp\ 8\delta)\cos \tfrac{1}{2}\pi\,(l - m) \\ &+ Z \exp\ 2\delta\,.\cos \tfrac{1}{2}\pi\,(l - m) + Z \exp\ 6\delta] \\ \equiv -\,(192e/b)\ \ &\phi_s\,(\lambda, t) \end{aligned} \tag{12}$$

where $\phi_s\,(\lambda, t)$ is the expression in square brackets multiplied by $-\lambda/12$ since $b = \lambda a$

Owing to the presence of the exponential factor this series $\phi_s\,(\lambda, t)$ is rather quickly convergent for the values of λ and t considered, and its evaluation involves no serious difficulty The values of $\phi_s(\lambda, t)$ for the values of λ and t considered are given in Table III

Table III —Values of $\phi_s\,(\lambda, t)$

t	$\lambda = 0$	0 05	0 10	0 15	0 20	0 25
1 4	0	0 000 038	0 000 303	0 001 012	0 002 360	0 004 431
1 6	0	50	400	1 351	3 184	6 106
1 8	0	59	478	1 637	3 928	7 678
2 0	0	65	531	1 848	4 528	9 045
2 2	0	66	557	1 975	4 953	0 010 144
2 4	0	66	554	2 012	5 190	10 941
2 6	0	62	525	1 960	5 236	11 422
2 8	0	54	469	1 822	5 092	11 584
3 0	0	43	389	1 603	4 766	11 435
3 2	0	29	286	1 305	4 266	10 964

§ 6 *Potential of the Neutral Groups in the Central Plane $z = 0$*

§ 6 1 A group of charges G_1 (fig 2) can be resolved into four times the sum of groups $\frac{1}{4}G_3$ and G_0 (fig 2), the position vectors of the vertices of these groups, relative to their centres, being respectively $\pm\lambda\mathbf{a}_1$, $\pm\lambda\mathbf{a}_2$, $\pm\lambda\mathbf{a}_3$ and $\pm\lambda(\mathbf{a}_1 - \mathbf{a}_3)$, $\pm\lambda(\mathbf{a}_2 - \mathbf{a}_3)$, $\pm\lambda(\mathbf{a}_1 - \mathbf{a}_2)$

The potential at P of a group $\frac{1}{4}G_3$ at the point $m\mathbf{a}_1 + n\mathbf{a}_2$ relative to P is that of a charge $6e$ at a distance r from P, where $r = ka$ and

$$k^2 = m^2 - mn + n^2$$

and of six charges $-e$ at distances from P whose squares are the following multiples of a^2 —

$$(m \pm \lambda)^2 - (m \pm \lambda)n + n^2 = k^2 \pm \lambda(2m - n) + \lambda^2$$
$$m^2 - m(n \pm \lambda) + (n \pm \lambda)^2 = k^2 \pm \lambda(2n - m) + \lambda^2$$
$$(m \pm \lambda)^2 - (m \pm \lambda)(n \pm \lambda) + (n \pm \lambda^2) = k^2 \pm \lambda(m + n) + \lambda^2$$

Hence, the potential of a $\frac{1}{4}G_3$ group (m, n) is

$$\rho_{m,n} = \frac{e}{ka}\left\{6 - \left(1 + \frac{\pm\lambda(2m - n) + \lambda^2}{k^2}\right)^{-\frac{1}{2}} - \left(1 + \frac{\pm\lambda(2n - m) + \lambda^2}{k^2}\right)^{-\frac{1}{2}} - \left(1 + \frac{\pm\lambda(m + n) + \lambda^2}{k^2}\right)^{-\frac{1}{2}}\right\},$$

there being really seven terms inside the bracket corresponding to the alternative upper and lower (+ and −) signs The quantity in the bracket can be expanded as a power series in λ The resulting expression for the potential of this $\frac{1}{4}G_3$ group (m, n) is, therefore, as follows, correct to the power λ^6 —

$$\rho_{m,n} = -\frac{3e}{2a}\left\{\frac{\lambda^2}{k^3} + \frac{9}{16}\ \frac{\lambda^4}{k^5} + \frac{281}{128}\ \frac{\lambda^6}{k^7} - \frac{231}{128}\ \frac{27}{2}\ \lambda^6\left(\frac{m^2}{k^9} - \frac{2m^4}{k^{11}} + \frac{m^6}{k^{13}}\right)\right\} \quad (13)$$

Similarly, the potential of a group G_0 at the same net-point (m, n) is given by

$$\sigma_{m,n} = \frac{3e}{2a}\left\{\frac{3\lambda^2}{k^3} + \frac{9}{16}\ \frac{(3\lambda^2)^2}{k^5} - \frac{181}{128}\ \frac{(3\lambda^2)^3}{k^7} + \frac{231}{128}\ \frac{27}{2}\ (3\lambda^2)^3\left(\frac{m^2}{k^9} - \frac{2m^4}{k^{11}} + \frac{m^6}{k^{13}}\right)\right\}, \quad (14)$$

where the ratio λ is replaced by $\lambda\sqrt{3}$, because the size of the hexagonal group G_0 is $\sqrt{3}$ times that of $\frac{1}{4}G_3$ Apart from this, the difference between the expansions for the two groups arises because of their different orientations relative to the network, and the difference in the signs of the charges

The potential at P of a G_1 group at the given net point $(m\ n)$ is $4(2\rho_{m,n}+\sigma_{m,n})$ The potential of the whole set of G_1 groups in the central plane is obtained by summing $4(2\rho_{m,n}+\sigma_{m,n})$ for all positive and negative integral values of m and n This summation can be simplified because the network of groups can be divided into six exactly similar sectors and the net points in one sector are represented by the values of n from 0 to $m-1$ m itself varying from 1 to infinity The potential for the groups in one sector is therefore obtained by summing the expression $4(2\rho_{m,n}+\sigma_{m,n})$ for these values of m and n Consequently, the potential for the whole set of neutral groups in the central plane is

$$V_\gamma = 24\sum_{m=1}^{\infty}\sum^{m-1}(2\rho_{m,n}+\sigma_{m,n}) \tag{15}$$

§ 6 2 To render the summed power series in λ suitably convergent the values of $\rho_{m,n}$ and $\sigma_{m,n}$ are calculated separately for the points $(m\ n)$—(1 0) (2 0) and (2 1) The corresponding part of $24\Sigma\Sigma(2\rho_{m,n}+\sigma_{m,n})$ is given by

$$\begin{aligned}24(2\rho_{1,0}+2\rho_{2,0}+2\rho_{2,1}) - (48e/a)\{&(6-2(1-\lambda+\lambda^2)^{-\frac{1}{2}}\\ &\quad -2(1+\lambda+\lambda^2)^{-\frac{1}{2}}-2(1-\lambda^2)^{-1})\\ &+(2\sqrt{3}-2(3-3\lambda+\lambda^2)^{-\frac{1}{2}}\\ &\quad -2(3+3\lambda+\lambda^2)^{-\frac{1}{2}}-2(3+\lambda^2)^{-\frac{1}{2}})\\ &+(3-2(4-2\lambda+\lambda^2)^{-\frac{1}{2}}\\ &\quad -2(4+2\lambda+\lambda^2)^{-\frac{1}{2}}-1(4-\lambda^2)^{-1})\}\end{aligned}$$

together with—

$$\begin{aligned}24(\sigma_{1,0}+\sigma_{2,0}+\sigma_{2,1}) - -(24e/a)\{&(6-2(1-3\lambda+3\lambda^2)^{-\frac{1}{2}}\\ &\quad -2(1+3\lambda+3\lambda^2)^{-\frac{1}{2}}-2(1+3\lambda^2)^{-\frac{1}{2}})\\ &+(2\sqrt{3}-2(3-3\lambda+3\lambda^2)^{-\frac{1}{2}}\\ &\quad -2(3+3\lambda+3\lambda^2)^{-\frac{1}{2}}-2\sqrt{3}\,(3-3\lambda^2)^{-1})\\ &+(3-2(4-6\lambda+3\lambda^2)^{-\frac{1}{2}}\\ &\quad -2(4+6\lambda+3\lambda^2)^{-\frac{1}{2}}-2(4+3\lambda^2)^{-\frac{1}{2}})\}\end{aligned}$$

To obtain the values of $\rho_{m,n}$ and $\sigma_{m,n}$ for the remaining groups it is necessary to calculate the values of—

$$\sum_{1}^{\infty}\sum_{0}^{1}1/k^p$$

where p takes the values 3 5 7 and also the values of

$$\sum_{m=3}^{\infty}\sum_{n=0}^{m-1}m^2/k^9,\qquad \sum_{m=3}^{\infty}\sum_{n=0}^{m-1}m^4/k^{11},\qquad\text{and}\qquad \sum_{m=3}^{\infty}\sum_{n=0}^{m-1}m^6/k^{13}$$

Now

$$\frac{1}{k^3} = \frac{1}{m^3}\left\{1 - \frac{n(m-n)}{m^2}\right\}^{-1}$$

$$= \frac{1}{m^3}\left\{1 + \frac{3}{2}\,\frac{n(m-n)}{m^2} + \frac{3}{2}\,\frac{5}{4}\,\frac{n^2(m-n)^2}{m^4} + \quad\right\}$$

It is therefore necessary to find $\sum_{n=0}^{m-1} n^r(m-n)^r \equiv \sum_{n=0}^{m} n^r(m-n)^r$ where r is an integer We have

$${}_mS_r = 1^r + 2^r + 3^r + \quad + m^r$$

$$= \frac{m^{r+1}}{r+1} + \tfrac{1}{2}m^r + \frac{r}{2!}B_1 m^{r-1} - \frac{r(r-1)(r-2)}{4!}B_2 m^{r-3} + \quad ,$$

where B_1, B_2, are Bernoulli's numbers if r is even, the last term in this expansion is a multiple of m, whilst if r is odd, the last term is a multiple of m^2

Using this expansion the summation $\sum_{n=0}^{m-1} n^r(m-n)^r$ can be expressed as a sum of multiples of negative integral powers of m, for all the necessary values of r Thus the double summation will involve $S'_p = \sum_{m=3}^{\infty} 1/m^p$, where p is an integer > 1 Values of $S_p = \sum_{m=1}^{\infty} 1/m^p$ are given in tables from which S'_p can be found

Thus,

$$\sum_{m=3}^{\infty}\sum_{n=0}^{m-1} 1/k^3 = \sum_{m=3}^{\infty}\sum_{n=0}^{m-1}\frac{1}{m^3}\left\{1 + \frac{3}{2}\,\frac{n(m-n)}{m^2}\right.$$

$$\left. + \frac{3\,5}{2\,4}\,\frac{n^2(m-n)^2}{m^4} + \quad\right\}$$

$$= S'_2 + \frac{3}{2}\left\{\frac{1}{6}S'_2 - \frac{1}{6}S'_4\right\} + \frac{3\,5}{2\,4}\left\{\frac{1}{2\,3\,5}S'_2 - \frac{1}{30}\,S'_6\right\}$$

$$+ \frac{3\,5\,7}{2\,4\,6}\left\{\frac{1}{4\,5\,7}\,.\,S'_2 + \frac{1}{2}\,\frac{1}{30}S'_6 - \frac{1}{42}S'_8\right\} +$$

$$= \frac{4}{3}S'_2 - \frac{1}{4}S'_4 - \frac{3\,5}{2\,4}\,\frac{1}{30}\,\frac{5}{12}S'_6 + \frac{3\,5\,7}{2\,4\,6}\,\frac{1}{42}\,\frac{7}{80}S'_8$$

$$+ \frac{3\,5\,7\,9}{2\,4\,6\,8}\,\frac{1}{30}\,\frac{631}{40\,56}S'_{10} -$$

$$= 0\ 5215\ 793,$$

on substituting for S'_2, S'_4,

Similarly,

$$\sum_{m=3}^{\infty}\sum_{n=0}^{m-1} 1/k^5 = \sum_{m=3}^{\infty}\sum_{n=0}^{m-1}\frac{1}{m^5}\left\{1+\frac{5}{2}\,\frac{n(m-n)}{m^2}\right.$$

$$\left.+\frac{5\ 7}{2\ 4}\,\frac{n^2(m-n)^2}{m^4}+\quad\right\}$$

$$=S'_4+\frac{5}{2}\left\{\frac{1}{6}S'_4-\frac{1}{6}S'_6\right\}+\frac{5\ 7}{2\ 4}\left\{\frac{1}{2\ 3\ 5}S'_4-\frac{1}{30}\ S'_8\right\}$$

$$+\frac{5\ 7\ 9}{2\ 4\ 6}\left\{\frac{1}{4\ 5\ 7}S'_4+\frac{1}{2}\ \frac{1}{30}\ S'_8-\frac{1}{42}\ S'_{10}\right\}+$$

$$=\frac{44}{27}S'_4-\frac{5}{12}S'_6-\frac{5\ 7}{2\ 4}\ \frac{1}{30}\ \frac{1}{4}S'_8+\frac{5\ 7\ 9}{2\ 4\ 6}\ \frac{1}{42}\ \frac{19}{80}S'_{10}$$

$$+\frac{5\ 7\ 9\ 11}{2\ 4\ 6\ 8}\ \frac{1}{30}\ \frac{137}{16\ 28}S'_{12}$$

$$= 0\ 0315\ 8328$$

In a similar manner it is found that

$$\Sigma\Sigma\, 1/k^7 = 0\ 0033\ \ 4468\ \ 7$$
$$\Sigma\Sigma\, m^2/k^9 = 0\ 0041\ \ 3865\ \ 7$$
$$\Sigma\Sigma\, m^4/k^{11} = 0\ 0051\ \ 5501\ \ 2$$
$$\Sigma\Sigma\, m^6/k^{13} = 0\ 0064\ \ 6466\ \ 2$$

Let

$$M = \Sigma\Sigma\,\frac{231}{128}\ \frac{27}{2}\left(\frac{m^2}{k^9}-\frac{2m^4}{k^{11}}+\frac{m^6}{k^{13}}\right)$$

Then, substituting the above values, $M = 0\ 0071\ \ 0179$, and, consequently,

$$-\frac{181}{128}\Sigma\Sigma\,\frac{1}{k^7}+M = 0\ 0023\ 722 \quad\text{and}\quad \frac{281}{128}\Sigma\Sigma\,\frac{1}{k^7}-M = 0\ 0002\ 408$$

§ 6 3 All the quantities involved in the $\rho_{m\ n}$ and $\sigma_{m,n}$ summations have thus been evaluated (*cf* equations (13) and (14)) Hence, the potential V_γ for the plane of G_1 groups is given by (*cf* equation (15))—

$$V_\gamma = 24\,(2\rho_{1,0}+2\rho_{2,0}+2\rho_{2,1}+\sigma_{1\ 0}+\sigma_{2,0}+\sigma_{2\ 1})+24\sum_{m=3}^{\infty}\sum_{n=0}^{m-1}(2\rho_{m\ n}+\sigma_{m,n})$$

$$= 24\,(2\rho_{1\ 0}+2\rho_{2\ 0}+2\rho_{2\ 1}+\sigma_{1,0}+\sigma_{2\ 0}+\sigma_{2\ 1})$$

$$-48(3e/2a)[\lambda^2(0\ 5215\ 793)+\lambda^4(0\ 0177\ 656)+\lambda^6(0\ 0002\ 408)]$$

$$+24(3e/2a)[3\lambda^2(0\ 5215\ 793)+9\lambda^4(0\ 0177\ 656)+27\lambda^6(0\ 0023\ 722)] \qquad (16)$$

The potential of the G_1 group of changes surrounding the point P, corresponding to $m = n = 0$, is not included in this expression (16)

Writing $b = \lambda a$ we can express (16) in the form

$$V_\gamma = (192e/b)\ \phi_\gamma(\lambda), \tag{17}$$

where $\phi_\gamma(\lambda)$ is the function obtained by multiplying the right-hand side of equation (16) by $\lambda a/192e$

The values of V_γ were calculated for a series of values of λ at intervals of 0 05 between 0 and 0 25 The values of $\phi_\gamma(\lambda)$ are given in Table IV, and they are the same for all the values of the other parameter t

Table IV — Values of $\phi_\gamma(\lambda)$

λ	0	0 05	0 10	0 15	0 20	0 25
$\phi_\gamma(\lambda)$	0	0 000 043	0 000 352	0 001 213	0 002 920	0 005 691

§ 7 *Potential of the Complete Composite Lattice of Charges* L_P

The potential of the complete composite lattice of charges L_P, at the point P, is obtained by adding the three sets of results corresponding to the three parts (α, β, γ) of the calculation, which are given by the formulæ (6), (12), and (17) (*cf* Tables II III, and IV) The final results are given by

$$V_\alpha + V_\beta + V_\gamma = -(192e/b)\ F(\lambda, t), \tag{18}$$

where the values of $F(\lambda, t)$ are given in Table V

Table V -Values of $F(\lambda, t)$

t	$\lambda = 0$	0 05	0 10	0 15	0 20	0 25
1 4	0	0 005 04	0 010 04	0 014 93	0 019 61	0 023 97
1 6	0	5 28	10 59	15 95	21 34	26 76
1 8	0	5 43	10 95	16 66	22 86	29 05
2 0	0	5 54	11 21	17 18	23 66	30 92
2 2	0	5 62	11 41	17 56	24 43	32 45
2 4	0	5 71	11 58	17 86	25 02	33 68
2 6	0	5 80	11 74	18 09	25 45	34 64
2 8	0	5 91	11 90	18 29	25 74	35 36
3 0	0	6 02	12 08	18 46	25 94	35 86
3 2	0	6 16	12 28	18 61	26 03	36 15

§ 8 *Electrostatic Potential Energy of the Carbonate Series of Crystals*

The electrostatic potential energy W of the carbonate crystals per molecule is given by (*cf* § 3 1)—

$$W = -(96e^2/b)\ F(\lambda, t) \tag{19}$$

This may be expressed in heat units per gram molecule of the crystal on (i) multiplying by the number of molecules per gram molecule and (ii) dividing by the mechanical equivalent of heat J

Thus the electrostatic potential energy per gram molecule for the carbonate series of crystals is given by

$$-(96e^2/b)\ F(\lambda,\ t)\ \ 6\ 062 \times 10^{23}/\mathrm{J}\ \text{calories},$$

where e is expressed in electrostatic units, b in centimetres, and $\mathrm{J} = 4\ \ 184 \times 10^7$ ergs per calorie

§ 9 *Calculation for the Nitrate Crystals*

The corresponding calculation for sodium nitrate will now be described As indicated in § 1.2, the sodium-nitrate lattice is of the same geometrical type as that of calcite, and hence the method need only be briefly stated The Ca and C ions in calcite are replaced by Na and N ions in sodium nitrate, consequently, the complete specification of the charges for the latter crystal is the same as the one given in § 2 4, except that the charges $4e$ of the C ions are replaced by the charges $5e$ of the N ions, and the charges $2e$ of the Ca ions by the charges e of the Na ions

Thus the electrostatic potential energy of sodium nitrate per molecule is ·

$$\mathrm{W}' = \tfrac{1}{2}\{5e\mathrm{V}_{\mathrm{N}}' - 3\ \ 2e\mathrm{V}_{\mathrm{O}}' + e\mathrm{V}_{\mathrm{Na}}'\},$$

where V_{N}', V_{O}', $\mathrm{V}_{\mathrm{Na}}'$ denote the electrostatic potential at the corresponding ions due to the remaining charges (*cf* § 3 1)

This equation may be written

$$\mathrm{W}' = \tfrac{1}{2}e\{5\mathrm{V}_{\mathrm{N}}' - 3\ \ 2\mathrm{V}_{\mathrm{O}}' + \mathrm{V}_{\mathrm{Na}}'\} \tag{3'}$$

Again, $\mathrm{W}'/\tfrac{1}{2}e$ may be interpreted as the potential at a point P due to a composite lattice L_{P}', built up in a similar manner to the corresponding one in calcite

This lattice consists of a system of charges at the lattice-points, and of neutral groups around the lattice-points, similar to that indicated in Table I, except that the charges $\pm\ 8e$ are replaced by charges $\pm\ 2e$, while the neutral groups, although they retain the same forms, are built up of different charges These groups may be denoted by G_1', G_2', $\tfrac{1}{2}\mathrm{G}_3$, and $\tfrac{1}{2}\mathrm{G}_4$ (fig 2)

§ 10 *Potential of the Composite Lattice of Charges* L'_{P}

§ 10 1 It is clear that the potential of the charges $\pm\ 2e$ at the lattice-points is simply one-quarter of that of the charges $\pm\ 8e$ in the case of calcite Thus the potential for these charges is

$$\mathrm{V}_e' = -(192e/c)\ \ \tfrac{1}{4}\phi_e(\lambda,\ t), \tag{6'}$$

where the values of $\phi_s(\lambda, t)$ are given in Table II, and the distance c defines the size of the NO_3 ionic group, being the distance from the N ion to the adjacent O ions

§ 10 2 To find the potential for the neutral groups in the planes $s \neq 0$, we have first to obtain expressions for the potential of a network of neutral groups G_1', G_2', $\frac{1}{2}G_3$, and $\frac{1}{2}G_4$ These can be found from the equations (9), (10), (11), and are as follows —

The potential of a network of $\frac{1}{2}G_3$ or $\frac{1}{2}G_4$ groups is

$$V = 4e/a \ \sum_{-\infty}^{\infty}{}' \sum \exp\ (\delta_0 z) \ \ \phi(l, m) \ \ \cos(l\xi - m\eta) \tag{9'}$$

The potential of a network of G_1' groups is

$$V = 4e/a \ \sum_{-\infty}^{\infty}{}' \sum \exp\ (\delta_0 z) \ \ \{5\phi(l, m) - 2\psi(l, m)\} \ \ \cos(l\xi - m\eta) \tag{10'}$$

The potential of a network of G_2' groups is

$$V = 4e/a \ \sum_{-\infty}^{\infty}{}' \sum \exp\ (\delta_0 z) \ \ \{3\phi(l, m) - \phi(2l, 2m)\} \ \ \cos(l\xi - m\eta) \tag{11'}$$

It is convenient to write

$$5\phi(l, m) - 2\psi(l, m) = Y' \qquad \text{and} \qquad 3\phi(l, m) - \phi(2l, 2m) = Z'$$

As before, these formulæ can be combined so as to obtain the complete potential for all the neutral groups in all the planes above and below the central plane Omitting exponential terms beyond exp. 8δ, the potential of the whole set of neutral groups outside the plane $z = 0$ is given by

$$\begin{aligned} V_s' = (8e/a) \ \sum_{-\infty}^{\infty}{}' \sum \, [&X(\exp\ \delta + \exp\ 5\delta + \exp\ 7\delta) \cos \tfrac{2}{3}\pi(l - m) + X \ \exp\ 3\delta \\ &+ Y'(\exp\ 4\delta + \exp\ 8\delta) \cos \tfrac{2}{3}\pi(l - m) \\ &+ Z' \ \exp\ 2\delta \ \cos \tfrac{2}{3}\pi(l - m) + Z' \ \exp\ 6\delta] \\ \equiv -(192e/c) \ \ \phi_s'(\lambda, t), \end{aligned} \tag{12'}$$

where $\phi_s'(\lambda, t)$ is the expression in square brackets multiplied by $-\lambda/12$

The part of this expression which involves X is also included in the corresponding expression for calcite (*cf* equation (12)), and its value has therefore been evaluated The values of $\phi_s'(\lambda, t)$ for the values of λ and t considered are given in Table VI

§ 10 3 It is evident that a G_1' group of charges can be resolved into the sum of groups 10 ($\frac{1}{2}G_3$) and 4 G_0 (fig 2) Consequently the potential for the G_1' groups in the central plane is given by

$$V_\gamma' = 6 \sum_{m=1}^{\infty} \sum_{n=0}^{m-1} (10\rho_{m,n} + 4\sigma_{m,n}) \tag{15'}$$

Table VI —Values of $\phi_\beta'(\lambda, t)$

t	$\lambda = 0$	0 05	0 10	0 15	0 20	0 25
1 4	0	0 000 019	0 000 153	0 000 518	0 001 218	0 002 331
1 6	0	25	203	699	1 684	3 300
1 8	0	30	245	860	2 126	4 291
2 0	0	33	274	988	2 517	5 222
2 2	0	34	290	0 001 076	2 836	6 081
2 4	0	33	292	1 120	3 071	6 831
2 6	0	31	280	1 121	3 215	7 452
2 8	0	27	255	1 077	3 267	7 933
3 0	0	22	217	990	3 225	8 266
3 2	0	15	168	862	3 091	8 448

where $\rho_{m,n}$ and $\sigma_{m,n}$ are given by equations (13) and (14) respectively The values of $\rho_{m,n}$ and $\sigma_{m,n}$ for the points $(m, n) = (1, 0), (2, 0)$ and $(2, 1)$ are calculated separately as in the case of the carbonates

Equation (15') can be written in the form

$$V_\gamma' = (192e/c) \ \phi_\gamma'(\lambda) \tag{17'}$$

The previous calculations can be used, and the values of $\phi_\gamma'(\lambda)$ for the various values of λ are given in Table VII

Table VII —Values of $\phi_\gamma'(\lambda)$

λ	0	0 05	0 10	0 15	0 20	0 25
$\phi_\gamma'(\lambda)$	0	0 000 022	0 000 179	0 000 626	0 001 519	0 002 926

§ 11 *Electrostatic Potential Energy of the Nitrate Series of Crystals*

The electrostatic potential of the complete composite network of charges L_T' is obtained by adding the three sets of results given by equations (6'), (12') and (17'), and the final expression may be written

$$V_\alpha' + V_\beta + V_\gamma' = -(192e/c) \ F'(\lambda, t), \tag{18'}$$

where the values of $F'(\lambda, t)$ are given in Table VIII.

The electrostatic potential energy per molecule of the nitrate crystal is therefore given by

$$W' = -(96e^2/c) \ F'(\lambda, t) \tag{19'}$$

This may be expressed in heat units per gram molecule (*cf.* § 8)

Table VIII —Values of F′ (λ, t).

t	λ = 0	0 05	0 10	0 15	0 20	0 25
1 4	0	0 001 26	0 002 50	0 003 68	0 004 74	0 005 71
1 6	0	1 32	2 56	4 02	5 43	6 96
1 8	0	1 36	2 77	4 29	6 02	8 12
2 0	0	1 39	2 85	4 60	6 51	9 19
2 2	0	1 41	2 91	4 65	6 92	0 010 16
2 4	0	1 43	2 96	4 76	7 24	11 01
2 6	0	1 46	2 99	4 83	7 48	11 75
2 8	0	1 48	3 02	4 87	7 64	12 37
3 0	0	1 51	3 05	4 88	7 73	12 87
3 2	0	1 54	3 07	4 87	7 74	13 24

§ 12 *Graphical Representation of the Calculated Results*

§ 12.1. The value of F (λ, t) thus being known for various values of the two parameters λ and t (*cf* Table V), it is easy to construct, by graphical interpolation, any number of equipotential curves passing through points on a (λ, t) diagram for which F (λ, t) has a constant value The curves or contour lines give a detailed representation of the function F, and are shown in fig 3 by broken lines Similarly the broken lines in fig 4 give a representation of the function F′ (λ, t).

In applying these curves to the consideration of the equilibrium of an actual crystal, it will be postulated that the size of the CO_3 ion (determined by b, § 4.2) is fixed, and also the distance f (§ 2 6) between an O ion and an adjacent metallic ion These two conditions imply a relation between λ and t, since the constant ratio f/b is a function of λ and t, as follows —

We have by equation (2)

$$f^2 - d^2 + (\lambda^2 - \lambda + \tfrac{1}{3})\,a^2 \quad \text{and} \quad b = \lambda a, \quad d^2 = \pi^2 a^2/27t^2$$

Hence

$$k^2 \equiv \frac{f^2}{b^2} - 1 = \frac{\frac{1}{3} + \frac{\pi^2}{27t^2} - \lambda}{\lambda^2} \equiv \frac{s - \lambda}{\lambda^2} \quad \text{if} \quad s \equiv \tfrac{1}{3} + \frac{\pi^2}{27t^2}, \qquad (20)$$

so that if f and b, and therefore also k, are constant, the right-hand side must also be constant Configuration curves corresponding to various values of k have been drawn on fig 3 in full lines (and similarly, replacing b in equation (20) by c, in fig. 4); these correspond to configurations of a crystal in which f and b have any constant values consistent with the indicated value of k.

The electrostatic potential energy (per molecule) of the crystal is W, equal to — $(96e^2/b)$. F (λ, t), so that along any configuration curve it is a constant multiple of F (λ, *t*) The configuration curves consequently indicate how W varies in any given series of configurations of a crystal in which *f* and *b* are kept constant

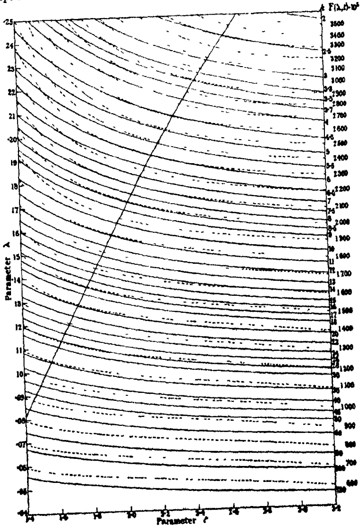
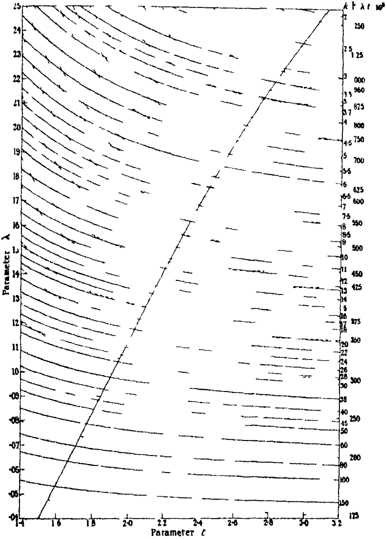


FIG. 3.


Parameter λ
25
24
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·05
·04
1·4
1·6
1·8
2·0
2·2
2·4
2·6
2·8
3·0
3·2
Parameter t
k
λt 10³
2
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3
3·3
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80
100
150
250
125
000
960
875
800
750
700
625
600
550
500
450
425
375
360
300
250
200
125

FIG 4

§ 12 2. It is clear that if a configuration curve touches an equipotential curve at a point C, say, this point corresponds to a configuration of the crystal in which the electrostatic potential energy is stationary Further, since the curvature of the equipotential curves is greater than that of the configuration curves, if we pass from C to a neighbouring point C′ on the same configuration curve, C′ will lie on an equipotential curve for which the value of F (λ, *t*) or F′ (λ, *t*) is smaller than that for the equipotential curve which passes through C Hence the point C of this configuration curve corresponds to a maximum value of F (λ, *t*), or F′ (λ, *t*), that is, the point C represents a configuration of the crystal in which the lost electrostatic potential energy is a maximum, so that the configuration is one of stable equilibrium As stated in § 1 3, it is assumed that the potential energy of the repulsive forces remains constant when, as here, the distances between immediately adjacent ions are not varied

There will be such a point C for every configuration curve, and the locus of these points can be found In figs 3 and 4, only a definite number of equipotential lines and configuration curves are drawn, although in reality there is an infinite number of each kind of curves, one of each passing through every point of the diagrams However, it is possible, by means of the curve shown, to sketch out the locus of the points C with some accuracy, and the

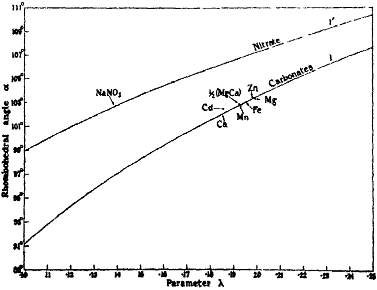

Fig. 5.

locus in the two cases is shown in the diagrams Each point on these loci corresponds to a pair of values of the parameters λ and t, which determine a stable equilibrium configuration of the crystal

Now the rhombohedral angle α of these crystals is not fixed by their symmetry but is given by*

$$\sin^2 \tfrac{1}{2}\alpha = 1/4s, \tag{21}$$

where s is defined in equation (20), and depends on t

Hence we can plot these loci on a new diagram with λ as abscissa and the rhombohedral angle α as ordinate, the resulting curves are shown in fig 5

§ 13 *Discussion and Comparison with Observation*

§ 13 1 Before comparing the results of our calculation with the observed data for the crystals, it is desirable to examine how far the physical assumptions underlying the analysis are justifiable, and in what way the various lengths a, f, b defining the crystal lattice are to be interpreted

§ 13 2 It has been assumed that the various atoms are completely ionised, in such a way that the O and Ca ions have eight electrons in their outer shell, while the C ion has lost its outer electrons It is not certain that this is so, especially in the case of the O ions, but Prof W L Bragg has recently pointed out† that even if the O electrons are partly shared with the C ion, they may circulate round the latter (because of the high positive charge) so quickly that they produce little or no effect of electrical screening

§ 13 3 But though the charge on the O ion may be effectively $-2e$, the strong and highly unsymmetrical field in which it is situated (owing to its proximity to the C^{++}_{++} ion) must distort it very much from the simple spherical form The question then arises whether it is legitimate to assume that its external electrostatic field can be that of a single point charge $-2e$, or whether it behaves as a combination of charge and doublets In the case of the C and Ca ions, round which the adjacent ions are grouped much more symmetrically than round the O ion, the assumption that they act as point charges, or, what is equivalent, spherical charge-distributions, is probably legitimate

Without fuller knowledge of the O ion than we possess, a conclusive answer to the above question is impossible It is certain that the O ion cannot be symmetrical, and Prof W L Bragg has cited* in this connection a calculation by Mr Hartree (based on spectroscopic, not crystal, data) indicating that the nucleus with the two inner electrons must be considerably displaced from the centre of the outer electronic system The calculation does not bear immediately on the present problem, because it relates to the displacement of the nucleus from its usually central position, when the ion is brought into a field equal to that of the C ion in the CO_3 group, but supposing the outer electronic system to be maintained unchanged The estimated displacement is 0·3 Å, which, though very small, is a considerable fraction of the distance (1·25 Å) between the C ionic centre and the O ionic nucleus, as measured by X rays In actual fact, of course, the outer electronic system will be much distorted from the approximately spherical form, but in so far as it can be said to have an effective centre of action, this is probably nearer to the C ion than the O nucleus, by an amount approximately equal to 0·3 Å, as in Mr Hartree's calculation

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* By an oversight, in the former paper by W L Bragg and S Chapman, this relation was quoted incorrectly as $\sec^2 \frac{1}{2}\alpha = 1 + s$, but the correct formula was used in the actual deductions.

† 'Institut International de Chimie Solvay,' Deuxième Conseil (1925) W L Bragg, "The X Ray Analysis of Crystal Structure"

§ 13·4 It is perhaps worth stating that if the oxygen ion is assumed to behave, as regards its external electrostatic field, like a conducting (insulated) sphere possessing a charge $-2e$, with its centre at the distance 1·25 Å from the C ion carrying a charge $4e$, then, if the diameter of the sphere be 1·25 Å, the positive and negative image charges of the C ion in the O ion will exactly neutralise the equivalent charge $-2e$ at the centre of the O ion, leaving a single equivalent (image) charge $-2e$ at the image-point, at a distance 0·94 Å from the C ion The value here assigned to the O ion is of reasonable order of magnitude Though this calculation obviously cannot conclusively justify the assumption that the O ion behaves electrostatically at external points like a single point charge $-2e$, distant 0·9 Å (approximately correct to 0·1 Å) from the C ion, yet it may be regarded as supporting the assumption. It will accordingly be supposed that the electrostatic centre O_e of the O ion in a CO_3 group is 0·9 Å distant from the centre of the C ion, viz, that

$$b = 0·9 \text{ Å} \qquad (CO_3 \text{ group})$$

§ 13.5 Another assumption involved in our analysis which requires some consideration is that the repulsive forces act from the same centre as the electrostatic forces This is legitimate in the case of the C and Ca ions, owing to the symmetrical distribution of their neighbouring ions, but it is unlikely to be true in the case of the distorted O ion Fortunately it is easy to examine how our calculation is affected by the supposition that the centre of action (O_r) of the repulsive force of the O ion does not coincide with O_e. By symmetry it must lie along the line CO_e, but we will suppose that $CO_r = b'$ where $b' \neq b$. Writing $b' = \lambda' a$, the virtual displacement of the lattice in which the change of potential energy is zero, both for the electrostatic and repulsive forces separately, is that for which an equipotential curve $F(\lambda, t) =$ constant, in fig. 3, touches a revised configuration curve corresponding to a series of states in which the distance Ca - O_r is constant, *i.e.* a configuration curve whose equation is (*cf.* equation 20)

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* *Loc. cit.*, 'Institut International de Chimie Solvay,' p 19.

$$k' \lambda'^2 = s - \lambda', \tag{22}$$

where k' is a constant.

Since the CO_3 ionic group is supposed to remain unchanged throughout the small displacement of the lattice, and throughout the different carbonates of the series, b' may be taken as a constant multiple of b, say pb and therefore λ' will be equal to $p\lambda$. The factor p may be supposed to lie within the range 0·9 to 1·2, corresponding to a range of b' from 0·8 Å to 1·1 Å.

Curves have been drawn on a (λ, t) diagram corresponding to fig. 3, satisfying the equation (22) (instead of (20)), for a series of constant values of k'. It is found that these revised configuration curves differ extremely little from those in fig. 3 and the locus of the points of tangency is not appreciably altered. Consequently, when $\lambda = 0·181$ (the appropriate value for calcite, taking $b = 0·9$ Å), the range in the equilibrium values of the rhombohedral angle, corresponding to the above range of b', is no more than 30′. We may therefore conclude that a slight disagreement between O_e and O_r is immaterial to our results.

We have also assumed that the repulsive forces between other than immediately adjacent ions are negligible (*cf.* § 1·3). Now in calcite the distance between adjacent Ca and O ions is shown by X-ray measurements to be approximately 2·4 Å, while the distance from an O ion to the next further Ca ion is approximately 3·42 Å, and to the nearest O ion not in the same CO_3 group is about 3·3 Å. Since the repulsive inter-ionic forces probably vary with the mutual distance, according to the inverse tenth power (roughly), it seems safe to make the above assumption.

§ 13.6. The above discussion may be summed up in the statement that the assumptions made in our calculation are approximately legitimate, provided that the correct position is assigned to O_e, the electrostatic centre of the O ion. It is concluded that the probable value of the distance CO_e or b is given correct to about 0·1 Å by:

$$b = 0·9 \text{ Å},$$

and investigation shows that our results are substantially unaffected by supposing O_r, the centre of the repulsive field of the O ion, to coincide with O.

The remaining distance involved in our calculation is a, the distance between the centres of consecutive C ions When this is given, the value of $b = \lambda/a$ is known, and this determines the equilibrium value of α in fig 5

For calcite the value of a has been determined by X-ray analysis owing to the symmetry of the C ion, there is no doubt that the distance thus measured represents the magnitude a here involved It appears that.

$$a = 4\ 96\ \text{Å}$$

Hence, taking $b = 0\ 9$ Å, $\lambda = 0\ 181$, and the corresponding theoretical value of α, deduced from fig 5, is 101° 40′ The corresponding values of α if b is assigned the values 0 8 Å and 1 0 Å are 99° 32′ and 103° 38′ The observed value of α is 101° 55′ The agreement between theory and observation may therefore be considered satisfactory In the original paper by W L Bragg and S Chapman, the value of b was taken as 1 25 Å, the distance from the C to the O nucleus the corresponding values of λ and α are 0 252 and 107° 48′, but the above discussion indicates that this interpretation of b is physically improbable

§ 13 7 If for calcite we invert the application of our theoretical calculations, and use them as a means of inferring λ from the observed rhombohedral angle α of calcite, we obtain the value 0 184, which, taking the above value of a, indicates that the correct value of b in the CO_3 ion is 0 91 Å

If, further, we assume that the CO_3 ion is the same in all the isomorphous series of carbonate crystals, from the known values of a in these crystals we can infer the value of λ corresponding to any given value of b, and hence can deduce the theoretical values of α. The value of b which gives the best fit for the series of carbonates is 0 92 Å (as compared with 0 91 Å from calcite only) The results calculated by taking $b = 0\ 92$ Å are given in the following Table, and the good accordance between the calculated and observed values shows that the theory can give an excellent account of the small change of rhombohedral angle from one member of the isomorphous series to the next The probable accuracy of the observed values of α is such that the small remaining discrepancies in this Table may be due to experimental error

§ 13 8 We next consider the nitrate case X-ray measurements on sodium nitrate have been made by W L Bragg* and Wykoff,† which show that

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* W L Bragg, 'Roy Soc Proc,' A, vol 89, p 468 (1914).

† R W G Wykoff, 'Phys Rev,' vol 16, p. 149 (1920).

Carbonate	Value of a	λ $b = 0\ 92$ Å	Calculated Values of α	Observed Values of α
$MgCO_3$	4 61	0 200	103° 28	103° 21 5
$ZnCO_3$	4 64	0 198	103° 18	103° 28
$FeCO_3$	4 70	0 196	103° 6	103° 4 5
$MnCO_3$	4 77	0 193	102° 52	102° 50
$\frac{1}{2}(MgCa)CO_3$	4 78	0 192	102° 44	102° 53
$CdCO_3$	4 92	0 187	102° 15	102° 30
$CaCO_3$	4 96	0 185	102° 4	101 55

the value of a *i e* the distance between adjacent N centres is 5 15 Å The value of λ is estimated to be about 0 25 the corresponding value of the distance c between an N ion and the O ions of the same group is 1 29 Å But on Kossel s view of the structure of the NO_3 group according to which the N ion has a five fold positive charge the size of the NO_3 group is likely to be smaller than that of the CO_3 group This view is supported by considerations of birefringence from which W L Bragg* estimates the distance c to be 1 09 Å It therefore seems that we may take this latter estimate as the more correct one though the two estimates do not necessarily refer to the same point in the O atom

For the purpose of the present paper the important point is the equivalent electrostatic centre of the O atom and owing to the fivefold positive charge of the N ion the distortion of the O ion is likely to be even greater in the case of the NO_3 group than in that of the CO_3 group This would draw the electro static centre of the O ion towards the N ion and an estimate of the resulting distance NO_3 ($= c$) obtained from an image calculation similar to that in § 13 4 but assuming the distance from the C ion to the centre of the O ion to be 1 10 Å gives a value of c about 0 70 Å The value of a in $NaNO_3$ being 5 15 Å, the corresponding value of λ will be 0 136 The corresponding value of α, as given by fig 5 (curve 1) is 102° 26′ and the observed value is 102° 42 5 The agreement is therefore satisfactory

If α is regarded as known and fig 5 (curve 1) is used to determine λ and thence c, the deduced value of c is 0 72 Å

§ 14 One of us (J Topping) has been in receipt of a grant from the Department of Scientific and Industrial Research

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* W L Bragg, 'Roy Soc Proc., A, vol 106, p 356 (1924)

Summary

(1) The details and detailed results of the calculation of the electrostatic potential energy of ionic lattices of the calcite type as used in a recent paper by W L Bragg and S Chapman are given

(2) The method and results of a similar calculation for an ionic lattice of the same geometrical form as in calcite but with different ionic charges such as occur in sodium nitrate are given

(3) These results are used to give a theoretical determination of the rhombohedral angle in a series of carbonate crystals of the calcite type and in sodium nitrate or alternatively to deduce from the observed rhombohedral angles the distance between the electrostatic centres of the oxygen ions in the CO_3 and NO_3 groups

The above applications by no means fully utilise the calculations of this paper which have an essential bearing on many other physical properties of the crystals considered Some of these involve the calculation of the potential energy of the repulsive forces between the ions It is hoped to deal with such further applications in later papers

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On Lightning

By G C Simpson D Sc F R S

(Received March 17 1926)

[Plates 1 and 2]

A lightning discharge is a discharge of electricity through a gas at atmospheric pressure and can take three forms —

(a) A discharge between a part of the atmosphere having a volume charge of electricity generally a cloud and the ground

(b) A discharge between two parts of the atmosphere each part having a definite volume charge of electricity, but of opposite signs

(c) A discharge from a part of the atmosphere having a volume charge into a part of the atmosphere in which no initial volume charge is present

In the first case the ground forms an electrode, but in the two latter cases the discharge does not pass between electrodes In most studies of the discharge of electricity through gases the conditions at the surface of the electrodes form an important part in the discussion, and so far as I know the mechanism of an electrodeless discharge at atmospheric pressure has not been described

In the following discussion the method in which electrical separation takes place in a thunderstorm is not considered, but the following assumptions are made --

(*a*) The mechanism of a thunderstorm results in the concentration of electricity of one sign in the form of a volume charge throughout an appreciable extent of the atmosphere

(*b*) The air is unable to withstand more than a certain definite electrical intensity , if that intensity is exceeded ionisation takes place

(*c*) The mobility of negative electrons is so great in comparison with the mobility of positive ions that the latter may be considered not to move to any appreciable extent , while the former move at a high velocity and are the chief vehicles of the transport of the electricity

Fig 1 is a diagrammatical representation of the field of force about a region of the atmosphere, A, containing a volume charge of electricity, say the cloud of a thunderstorm For simplicity the volume is represented as a sphere placed some distance above the ground, the latter being perfectly level and smooth

The region of greatest electrical intensity is obviously at B, the lowest point of the cloud There the air will " break-down " first and ionisation occur As soon as this happens the lines of force move towards the conducting region and in consequence the field there increases, especially at the upper and lower parts of the conducting region This is shown diagrammatically in fig 2

The increase of force causes further ionisation and the conducting region extends along the lines of force, both upwards into the cloud and downwards towards the earth, as shown in fig 3[*]

At first sight it would appear that this process would be followed whether the charge in A were positive or negative On closer study, however, this appears not to be the case

Let us assume that the stage represented in fig 3 has been reached when the cloud A is charged with positive electricity The end of the conducting channel is shown in fig 4 (*a*) , it is filled with positive electricity, because all the negative electrons have passed rapidly along the channel towards the positively charged cloud. The field, however, is very intense at the end of the channel where the lines of force leave it and the region of greatest intensity is shaped something like that within the dotted line in fig 4 (*b*) Within this region ionisation takes place According to our assumption we need not consider how the ionisation takes place, all we need to know is that the intensity is greater than the minimum

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[*] J Larmor and J S. B. Larmor, 'Roy Soc. Proc,' A, vol. 90, p. 312 (1914).

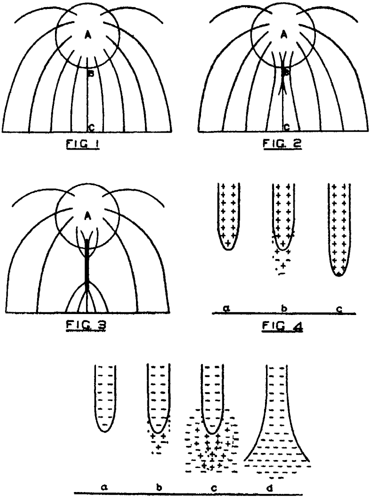

FIG 1 FIG. 2

FIG. 3 FIG 4

FIG. 5

Figs 1-5

intensity under which ionisation takes place in free air This intensity was obviously reached at the moment the discharge started near the cloud, and since then the intensity at the end of the channel has been steadily increasing as the channel lengthened

Ionisation will therefore take place, as indicated in fig. 4 (*b*), by the plus and minus signs, but the negative electrons are at once drawn into the channel and pass upwards into the cloud The ionised region in this way becomes filled with positive electricity and becomes indistinguishable from the remainder of the channel In other words the channel has lengthened, as shown in *fig* 4 (*c*), and the process once started will continue A number of things have, however, to be noticed In the first place, if there is any irregularity at the end of the channel a local increase or decrease of the force will result The discharge will tend to follow each of the directions in which the irregularity causes local maxima of force, and to avoid the minima There will, therefore, be considerable tendency for the end to bifurcate In fact a single straight discharge requires very uniform conditions which are not likely to occur often The normal condition of discharge will be a branched discharge, each branch continuing with a sharp point until it, in its turn, bifurcates

Secondly, it will be noticed that there is a sharp boundary to the channel of the discharge As soon as ionisation has occurred the negative electrons move at once into the channel, and as the positive ions do not move appreciably, there is little or no *spreading of electricity from the ionised channel into the surrounding air* The air is, therefore, practically unaffected outside the channel in which ionisation actually takes place

Thirdly, as the channel bores its way through the air, the negative products of the ionisation move along the channel towards the cloud, where the positive charge, which has been the cause of the discharge, is situated In other words, the discharge drains negative electricity out of the air through which it passes, and this may supply sufficient electricity to neutralise the greater part of the initial positive charge on the cloud As soon as this occurs the electrical intensity at the end of the channel decreases, and the discharge may come to an end while the channel is still far from the ground

We will now consider the case in which the charge on the cloud is negative, and assume that in this case also the discharge has proceeded as far as the stage shown *in fig* 3 *Fig* 5 (*a*) shows the end of the channel filled with negative electricity Again, the strongest field is at the point of the channel where ionisation takes place, fig 5 (*b*) So far the process is the same as with the positive charge, but now a difference takes place, the negative electrons are driven out of the ionised region into the surrounding un-ionised air, in doing so they extend the region of ionisation far beyond the boundary where the initial field was strong enough to cause a break-down of the air They also continue to move into the surrounding region after they have lost their power of ionisation This is shown diagrammatically in fig 5 (*c*) in which the region within the dotted curve corresponds with the similar region in fig 4 (*b*), while the region between the dotted curve and the broken curve indicates where the electrons, driven out of the former region, have ionised the air Outside this region there is another region containing the electrons which have moved forward without ionising the air The positive ions have not moved but negative electrons flow out of the channel and neutralise them The final state is shown in fig 5 (*d*) The channel no longer ends in a sharp point, but is blunted and surrounded by a mass of negative electricity This is obviously very different from the state of affairs from which we started (fig 5 (*a*)) The intense field at the point of the channel no longer exists and the tendency for the air to break-down in front of the discharge is greatly diminished and would very soon cease altogether It would appear from this that a negative discharge cannot form a channel but only a diffuse ionised region

Experimental support of these considerations is easily obtained, although it is impossible to reproduce the condition we have been describing in the laboratory, for we cannot produce a discharge without using electrodes which complicate the conditions, still, experiments were made which show that the main line of reasoning is correct

Two circular electrodes, each provided with a short piece of wire projecting from the edge, were placed on a photographic plate Each of these electrodes was connected to the outer layer of a Leyden jar, the inner layers of the two jars being connected to the terminals of a Wimshurst machine On causing a spark to pass between the terminals of the machine, an induced discharge took place from the two circular electrodes over the photographic plate. The result is shown in fig 6 (Plate 1) The electrode A received a positive charge The small piece of wire was intended to represent the channel depicted in fig 4 (*a*) We see that the discharge has left it in long, pointed and much-branched channels, which have proceeded far into the surrounding region. It will also be noticed that each channel has a sharp boundary and that the ends of all the channels are pointed The conditions are entirely different in the negative discharge from electrode B There the discharge has not proceeded along clear-cut channels, but has simply spread out in a diffuse cloud at the end of the wire *

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* Heavily condensed negative discharged over photographic plates frequently show branched channels These are, however, quite different from the channels associated with positive discharges. They simply connect points at which negative brush discharges occur and supply the electricity from the electrode to these brushes They cannot grow indefinitely

The electrical intensity must have been approximately the same at the two electrodes, but in one case the discharge has spread far from the electrode into the surrounding air, while in the other case the discharge has not spread appreciably farther than the small region in which ionisation occurred in consequence of the first intense field

Returning now to the thunderstorm problem we see that the condition represented in fig 3 would be possible if the cloud A had been positively charged but the discharge would probably have been along several branched channels instead of the single channel shown in the diagram On the other hand if the cloud had been negatively charged a channel would not have been formed at all As soon as the air had broken down in a small region (B of fig 2) owing to the intense field the negative electrons would have spread out in all directions, reducing the intensity and so preventing the formation of a channel

To develop these ideas further the following experiment was made A brass ball, to represent a cloud was mounted opposite a brass plate to represent the earth, the ball and the plate being connected to the poles of a Wimshurst machine The brass ball half an inch in diameter, was mounted on the end of a brass rod pivoted so that the ball could describe a circle in a plane at right angles to the brass plate The arm was first set at right angles to the plate so that the ball was at the minimum distance from the plate about 1½ inches and a discharge made The arm was then rotated slightly so increasing the spark gap, and another discharge made This was repeated the result being a series of discharges each having a longer spark gap

When the ball was positively charged and at its minimum distance from the plate, sparks passed between the ball and the plate These sparks were branched towards the plate As the spark gap was lengthened, branched discharges continued from the ball towards the plate, but did not reach it A photograph of the effect is shown in fig 7 (Plate 1) which is strongly reminiscent of typical photographs taken during thunderstorms

When the ball was charged negatively the conditions were entirely different If the ball was sufficiently near the plate strong unbranched discharges passed

in length; but immediately they reach a part of the electrical field not already occupied by a brush discharge they give rise to a new brush discharge It must be remembered that a discharge over a photographic plate is a three-dimensioned discharge constrained to two dimensions In the absence of the plate the negative discharge would be a mass of small brush discharges around the electrode each connected to the electrode by these short thick channels. This is clearly seen in Toepler's important discussion 'Ueber den inneren Aufbau von Gleitbüscheln und die Gesetze ihrer Leuchtfäden,' 'Annalen der Physik,' vol 53, p. 217 (1917)" between the ball and the plate but when the spark gap was lengthened these ceased entirely and there was only a small brush discharge on the surface of the ball In this case there was no intermediate discharge between a simple brush and a spark to the plate see fig 8 (Plate 1)

The spark discharge with the ball negatively charged seems to be caused as follows —

The brush discharge cannot carry off the electricity so rapidly as it reaches the ball and the intensity of the field between the ball and the plate increases It is well known that at the surface of an electrode a discharge can start before the electrical field in the adjacent air has reached the intensity necessary for the air to break down in the absence of the electrode Thus as the electrical intensity between the ball and plate increases a stage is reached when a discharge can start at the surface of the plate This is a positive discharge which rapidly grows along a channel towards the ball The channel however as it grows and approaches the ball gets into stronger and stronger fields thus the discharge once started at the plate rapidly passes to the ball as an intense spark The discharge follows the lines of force but in this experiment all the lines of force converge into the small ball there is therefore very little spreading of the lines of force at the end of the discharge as it proceeds from the plate towards the ball Hence there is little or no tendency for the discharge to branch and none of the photographs of this experiment showed branches If however the ball had been more extensive and composed of a badly conducting material there is little doubt that branching would have taken place as the discharge approached the surface of the ball The branching would however, have been towards the ball and not as in the case of a positively charged ball towards the plate

Thus these experiments confirm our conclusion that branched discharges "into the air are possible from positively charged clouds but not from negatively charged clouds Discharges may pass between the earth and both positively and negatively charged clouds but in each case the branching will be away from the seat of the positive charge A discharge from a positively charged cloud will have the branches turned away from the cloud while a discharge from a negatively charged cloud—which discharge must always start from the earth or from a positively charged cloud—will have the branches directed towards the cloud

Having reached these conclusions I decided to examine as many photographs of lightning as I could in order to determine the charge on the cloud from the direction of the branching I therefore wrote to ' Nature asking for photo

Fig 6

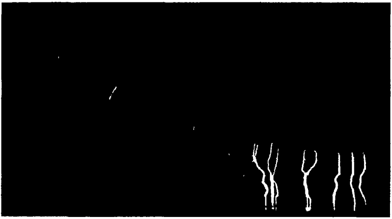

Fig 7

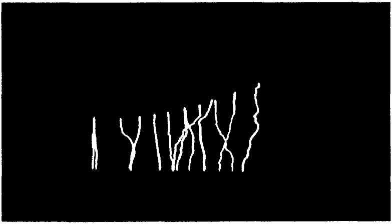

Fig 8

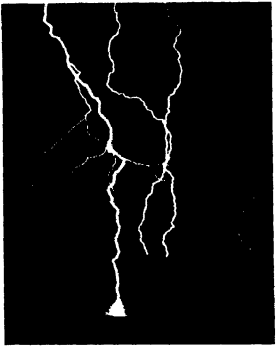

Fig 9

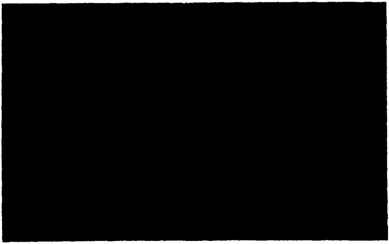

Fig 10

graphs to be loaned to me This letter was reproduced in the popular press and in response I received 121 photographs to examine The Royal Meteorological Society has a large collection of photographs of lightning and there are a few in the library of the Meteorological Office In all I examined 442 photographs

I was considerably surprised to find that while 242 of these photographs showed branched discharges with the branches directed away from the cloud only three two of which are very doubtful had the branches directed towards the cloud There were unbranched discharges on 173 photographs some of which contained also branched discharges But there is a difficulty here The branches on a branched discharge are always much less intense than the main discharge In consequence a branched discharge photographed through cloud or rain may appear unbranched simply because the branches are obscured while the main discharge can be seen An example of this is shown in fig 9 (Plate 2) Here four flashes have been photographed simultaneously all obviously proceeding from the same cloud It is to be presumed that there was heavy rain at the time The flash in the foreground is clearly branched away from the cloud The two flashes in the middle distance are partly obscured by the rain but branches in the same direction can be faintly seen The flash in the background is so much obscured by the rain that it is relatively faint and no sign can be seen of the branches but there can be little doubt that it was branched away from the cloud equally with the others Many of the unbranched discharges were faint and I have little doubt that a large proportion of them were branched away from the cloud although the branches could not be seen on the photographs

The 442 photographs may be classified as follows it being remembered that if several types of discharge appear on one photograph that photograph will be counted in more than one class —

Class I —Photographs showing definite branches away from the cloud	242
Class II —Photographs showing branches towards the cloud	3
Class III —Photographs showing unbranched discharges	173
Class IV —Photographs showing meandering and other discharges not classified above	134

We can say definitely that flashes of Class I indicate positively charged clouds and flashes of Class II negatively charged clouds Flashes of Class III may indicate either positive or negative clouds but in view of the fact stated above that the absence of branches is frequently due to the branches being obscured by clouds and rain, the large majority of them probably belong in reality to Class I In any case it is almost certain that if we allot half to positive and half to negative clouds we shall over-estimate the number of negative clouds Nothing definite regarding the sign of the clouds could be deduced from photographs of Class IV

So far as the evidence of these photographs go there can be little doubt that a large preponderance of the low clouds with which visible discharges are associated are positively charged Dividing the unbranched discharges into equal parts, as suggested above, we find that 328 photographs indicate positive clouds while only 89 indicate negatively charged clouds , this is a ratio of nearly 4 to 1, and even this, I am inclined to believe, is too small a ratio

In view of the exceptional nature of flashes branched towards the clouds, a few words might not be out of place about the three examples found in this collection of photographs In two of them there is reason to believe that the apparent branching towards the cloud is not real but only an effect of perspective They could equally well be explained by ordinary branched discharges directed towards the camera from some distant point in the sky, for the branches appear to radiate from a centre, some branches going upwards and some downwards In view of the doubt they have been included in Class II , but alone they would carry very little weight The third photograph in this class is most remarkable, and in view of its unique nature it is reproduced here as fig 10 (Plate 2)

This photograph, which is in the collection of the Royal Meteorological Society, is so remarkable that I long doubted its genuineness and thought that it might be the photograph of a picture On the back there is the statement " Taken on the night of June 28/92," while the name of the photographer appears on the front as "I Craik, Canterbury and Herne Bay," evidently a professional photographer To get information I wrote to the address given, but my letter was returned through the Dead Letter Office While seeking for internal evidence of its genuineness I examined the picture with a magnifying glass and then noticed that every rope of the rigging of the boat in the foreground is duplicated If the picture had been painted this would not have been done , but if a camera had been held while the shutter was opened, so that it moved slightly between two of the flashes, the effect—which is frequently seen in photographs of lightning —would have been produced I therefore now have no doubt that the photograph is genuine

So far we have only considered the discharge outside the cloud The same reasoning must also apply to the part of the discharge which distributes the electricity within the cloud Taking the case of a positively charged cloud first, after the air has broken down at the edge of the charged region the channel starts to develop in both directions But the part of the discharge directed towards the interior of the cloud is a negative discharge and, therefore, cannot produce a channel The negative electricity, which flows along the channel towards the cloud, escapes into the cloud in the form of a diffuse cloud of negative electrons The electrons soon become negative ions, after which they can only move relatively slowly towards the positive electricity in the remoter parts of the cloud There is, therefore, an accumulation of negative electricity around the end of the channel within the cloud This is shown diagrammatically in fig 11 The accumulation of negative electricity reduces the field at the mouth of the channel and prevents further flow In other words, the end of the channel becomes blocked and the discharge along the channel ceases But the

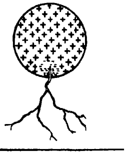

FIG. 11

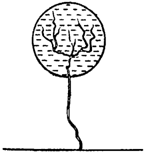

FIG 12

accumulation of negative electricity is constantly being dispersed under the electrical field and by eddies within the cloud As the accumulation disappears the field is again established and flow of electricity commences again along the original channel if the ions within it have not had time to recombine entirely Thus the flow along the channel will be intermittent and this is exactly what has been found to be the case The intermittent nature of lightning discharges has been much studied in a series of valuable papers by Prof Walter, of Hamburg

It has been shown that a discharge between the earth and a negatively charged cloud takes the form of a positive discharge which starts at the ground Within the cloud the channel branches and the branches extend rapidly into all parts of the cloud, discharging the greater part of the negative volume charge as the result of a single flash This is indicated in fig 12 Another discharge cannot start until the intense field has been again established right to the surface of the earth and this will take some time A discharge of this nature is not likely therefore to be intermittent * If this reasoning is correct, lightning flashes between the earth and a negatively charged cloud will be much more intense than flashes to a positively charged cloud, although the two clouds may be charged to the same intensity In fact, one would expect on this reasoning that discharges from positively charged clouds would be frequent but weak, while discharges from negatively charged clouds would be infrequent but very strong

These considerations are supported by the flashes shown in fig 10 There can be little doubt that the flashes shown in the photographs were from the sea to a negatively charged cloud above The cloud, however, was so thin that the branching within the charged region of the atmosphere could be clearly seen Normally, the branched part would be within a thick cloud and therefore invisible, only the thick unbranched discharge below the cloud being visible

There is a type of lightning discharge, which starts in a cloud and then progresses so slowly across the sky that the eye can follow it with ease, in the same way that the path of a rocket can be seen I saw this phenomenon in Belgaum, in India, in the year 1907 There was a thunderstorm in the distance, the cumulus cloud of which stood up sharp against the sky From the lower part of the cloud a series of discharges took place, the discharges moving quite slowly in a horizontal direction to some considerable distance from the cloud The effect was as though coiled up ribbons were being thrown out of the cloud which unrolled as they moved away to the right There can be little doubt that the explanation is the following –

A positive discharge starts from the cloud , as it progresses it ionises the air in a narrow channel, sending the negative ions along the channel to the cloud But the rate at which the channel can grow depends on the rate at which the cloud can absorb the negative charge which reaches it. If it can absorb it quickly the channel can grow quickly, if it absorbs it too slowly the discharge ceases. But there may be an intermediate state in which the cloud can absorb just sufficient to keep the channel growing slowly without the discharge ceasing altogether In this case we should have lightning of the nature described Probably meandering lightning is also caused in some such way

For simplicity of treatment, discharges between a cloud and the earth only have been considered above , but obviously the same considerations apply to

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* All the photographs of intermittent lightning which I have seen are clearly branched away from the cloud, indicating that the cloud was positively charged.

discharges between clouds The discharge will start in the region of greatest electrical strain between the two clouds and travel as a branched discharge towards the negatively charged cloud. All the other consequences will follow naturally and need not be considered further here.

Summary

An explanation of the discharge of electricity through air at atmospheric pressure has been given which leads to the following conclusions —

(*a*) The conducting channel of a lightning flash originates in the region of maximum electric field and develops only in the direction of the seat of negative electricity

(*b*) A negatively charged cloud can only be discharged by a discharge which originates in a positively charged cloud or in the induced positive charge on the earth's surface

(*c*) A positively charged cloud may be discharged by discharges starting in the cloud and terminating either in the surrounding atmosphere or on the earth's surface

(*d*) If a lightning flash is branched the branches are always directed towards the seat of negative electricity

(*e*) The application of these conclusions to 442 photographs of lightning discharges reveals the fact that the preponderance of the lower clouds from which lightning discharges proceed are positively charged.

In conclusion I would like to express my thanks to all those who provided me with photographs of lightning to study, and in particular to the Royal Meteorological Society, who not only placed their fine collection of photographs at my disposal, but have also given me permission to publish here the unique photograph reproduced as fig 10 (Plate 2) ' I am also grateful to Prof Callendar, who kindly lent me a powerful Wimshurst machine for carrying out the experimental part of the work

A Review of Mr George W Walker's Magnetic Survey (1915).

By SIR ARTHUR SCHUSTER, F R S

(Received March 25, 1926)

1 Recent magnetic surveys, whether extended over the whole surface of the earth or confined to limited areas, seem to indicate that the observed magnetic forces are not entirely deducible from a potential function, the curl round a vertical axis having finite value The evidence is strong, and were it not for the extreme difficulty of finding a rational explanation it would probably be accepted as decisive Exclusive of unknown effects, the observations can only be accounted for by electric currents cutting the surface of the earth Such currents are indeed known to exist, but their intensity is only an insignificant fraction of that deduced from the magnetic forces Grave objections may also be raised against the alternative explanation assigning the effect to a penetrating corpuscular radiation

The principal argument in favour of the real existence of an earth-air current is supplied by the world surveys, which show an apparent regularity depending on latitude, being upwards in the polar regions and generally downwards in lower altitudes According to Dr Bauer, upward currents of the same order of magnitude are found in terrestrial districts within the United States Rücker and Thorpe obtained no decisive results in Great Britain, while in the districts covered by Mr Walker's survey, he gives six with currents agreeing in direction with that found by Dr Bauer and two in the opposite direction

It appears to me that the most hopeful method of obtaining a decisive test is to examine the distribution of the magnetic forces over an area sufficiently small to justify a linear representation of their variation This will at the same time facilitate the taking of simultaneous observations at each pair of the selected stations

In order to form some judgment of the possibility of obtaining the desired accuracy, I have found it necessary to re-calculate the whole of Mr Walker's material, applying the method of least squares instead of the simplified procedure first introduced by Rücker and Thorpe and adopted by Walker The better agreement so obtained between the calculated and observed forces may not be very important, but the more rigorous method of calculation has collateral advantages which seem to me to outweigh the increased labour involved It excludes arbitrary assumptions, it affords convenient checks on the calculations, and it so happens that the magnetic problem adapts itself exceptionally well to treatment by it With the help of calculating machines the additional numerical work is by no means formidable

2 We express the North and West Forces by —

$$\left.\begin{aligned} N &= N_0 + \alpha(\lambda - \lambda') + \beta(l - l') \\ W &= W_0 + a(\lambda - \lambda') + b(l - l') \end{aligned}\right\}, \tag{1}$$

where λ' and l' are conveniently selected latitudes and longitudes Each of these equations contains three quantities to be determined and each observing station furnishes one equation

Introducing the notation

$$\left.\begin{aligned} &A' = \Sigma(\lambda - \lambda')^2, \quad &&B' = \Sigma(l - l')^2, \quad &&C' = \Sigma(\lambda - \lambda')(l - l') \\ &F' = \Sigma N(\lambda - \lambda'), \quad &&G' = \Sigma N(l - l') && \\ &\delta = \Sigma(\lambda - \lambda'), \quad &&\epsilon = \Sigma(l - l'), \quad &&U = n^{-1}\Sigma N \end{aligned}\right\}, \tag{2}$$

the normal equations obtained in the usual way are

$$\left.\begin{aligned} nU &= N_0 n + \delta\alpha + \epsilon\beta \\ F' &= N_0\delta + A'\alpha + C'\beta \\ G' &= N_0\epsilon + C'\alpha + B'\beta \end{aligned}\right\} \tag{3}$$

Eliminating N_0 between the first and second and between the first and third of these equations and writing

$$\left.\begin{aligned} &A = A' - n^{-1}\delta^2, \quad &&B = B - n^{-1}\epsilon^2, \quad &&C = C' - n^{-1}\delta\epsilon \\ &F = F' - U\delta &&G = G' - U\epsilon && \end{aligned}\right\}, \tag{4}$$

the equations reduce to

$$F = A\alpha + C\beta,$$

$$G = C\alpha + B\beta,$$

and finally

$$\alpha = \frac{BF - CG}{AB - C^2}, \qquad \beta = \frac{AG - CF}{AB - C^2} \tag{5}$$

Similarly for the West Forces

$$a = \frac{BD - CE}{AB - C^2}, \qquad b = \frac{AE - CD}{AB - C^2}, \tag{6}$$

D and E taking the place of F and G when N and W are interchanged These calculations are simplified if λ' and l' are respectively the average values of the latitudes and longitudes of the stations, so that δ and ϵ are equal to zero We shall denote the mean latitude and longitude by λ_0 and l_0 and refer to the point having these co-ordinates as the "central" point

A further simplification results when the observing stations are placed symmetrically with respect to the central point, in which case $C = 0$. The expression for the coefficients then takes the simple form

$$\left.\begin{array}{ll} \alpha = F/A, & \beta = G/B \\ a = D/A, & b = E/B \end{array}\right\} \qquad (7)$$

Local circumstances will, in general, prevent the condition $C = 0$ from being exactly fulfilled in the first choice of stations, but this may then be secured by an additional station being introduced anywhere on the hyperbola defined by

$$\Sigma\,(\lambda - \lambda_0)\,(l - l_0) = -C$$

It may further be inconvenient to introduce additional decimal places in order to satisfy the condition $\delta - \epsilon = 0$, but it is always easy to obtain sufficiently accurate values to be able to treat these quantities as small, so that their squares and product in (4) may be neglected.

3. We now proceed to show how a number of regions for which the coefficients have been determined may be combined and reduced to a common centre. We denote by Λ and L the averages of the latitudes and longitudes of all stations in the area, and desire to find the value of A, B, C, etc., for the whole area in terms of their values in the separate Districts. If the average latitude and longitude in the *m*th District is respectively λ_m and l_m while A_m is the District value of A, the contribution of the *m*th District to A is

$$\begin{aligned} \Sigma\,(\lambda - \Lambda)^2 &= \Sigma\,\{(\lambda - \lambda_m) + (\lambda_m - \Lambda)\}^2 \\ &= \Sigma\,(\lambda - \lambda_m)^2 + \Sigma\,(\lambda_m - \Lambda)^2 + 2\Sigma\,(\lambda - \lambda_m)\,(\lambda_m - \Lambda) \end{aligned}$$

Within each District $\lambda_m - \Lambda$ is constant and $\Sigma\,(\lambda - \lambda_m) = 0$, so that the contribution of the *m*th District to A is

$$\Sigma\,(\lambda - \Lambda)^2 = A_m + n_m\,(\lambda_m - \Lambda)^2,$$

when n_m stands for the number of stations in the District. The complete value of A is found by summing up the contributions of the separate Districts. The same reasoning holds for the values of B, C, etc. We thus obtain

$$\begin{aligned} A &= \Sigma A_m + \Sigma n_m\,(\lambda_m - \Lambda)^2, \\ B &= \Sigma B_m + \Sigma n_m\,(l_m - L)^2, \\ C &= \Sigma C_m + \Sigma n_m(\lambda_m - \Lambda)\,(l_m - L), \\ F &= \Sigma F_m + \Sigma n_m U_m\,(\lambda_m - \Lambda), \\ G &= \Sigma G_m + \Sigma n_m U_m\,(l_m - L), \\ D &= \Sigma D_m + \Sigma n_m R_m\,(\lambda_m - \Lambda), \\ E &= \Sigma E_m + \Sigma n_m R_m\,(l_m - L) \end{aligned}$$

U_m and R_m are the average values of N and W in the mth region, and the sums are taken with respect to m.

4. Equations (1) determine the lines along which the two components of magnetic forces are equal, but we obtain a clearer view of the distribution of the forces by expressing the result of terms of the direction of the normals to the lines of equality and the rate of variation along these. The coefficients being negative in the majority of cases, it is convenient to measure the angles from the line drawn towards the South in anti-clock wise rotation. We put for the North component

$$\cos\theta = \frac{-\alpha}{\sqrt{\alpha^2+\beta^2}}, \qquad \sin\theta = \frac{-\beta}{\sqrt{\alpha^2+\beta^2}}, \qquad \tan\theta = \beta/\alpha,$$

and for the West component

$$\cos\phi = \frac{-a}{\sqrt{a^2+b^2}}, \qquad \sin\phi = \frac{-b}{\sqrt{a^2+b^2}}, \qquad \tan\phi = b/a$$

The sign attached to the trigonometrical functions are chosen so as to give a positive value to the direction of *increasing* North and West Force. It is to be noted that λ and l are expressed in minutes of arc and not in linear measure. The angles are therefore those applying to a map in which minutes of arc in latitude and longitude have equal length.

5. Having obtained the relevant coefficients, we apply them to determine the departures from the potential law. Without committing ourselves to any opinion as to their origin, it is convenient to express these departures in terms of the earth-air currents with which they may be associated. If R be the radius of the earth, N and W the components of magnetic force, the latter being positive towards the geographical West, the vertical current densities (i) in the upward direction are

$$4\pi R i \cos\lambda = \frac{dW\cos\lambda}{d\lambda} - \frac{dN}{dl} \tag{8}$$

In the application of this formula it is convenient to replace the circular measure by minutes of arc and to introduce $\gamma = 10^{-5}$ C.G.S. as unit of force. We must therefore write

$$\frac{dN}{d\lambda} = \sigma\alpha \times 10^{-5}, \qquad \frac{dW}{dl} = \sigma b \times 10^{-5},$$

where σ is the unit circular measure in terms of minutes of arc, i.e. $3{\cdot}4378 \times 10^3$. Equation (8) then reduces to

$$4\pi \times 10^5 R i \cos\lambda = \sigma(a\cos\lambda - \beta) - W\sin\lambda.$$

Finally we put $\pi R = 2 \times 10^9$ and introduce the factor 10^{11} in order to obtain the current density (I) in ampères per square kilometre We thus obtain ·

$$8I = 3{\cdot}4378(\alpha - \beta \sec \lambda) - W_0 \times 10^{-3} \tan \lambda \tag{9}$$

6 In determining the probable errors in the usual manner, we must give to that expression a somewhat extended meaning and include not only the actual errors of observation but all deviations from the linear law, whether due to the normal curvature of the lines of force or to local disturbances We must therefore expect the probable error to depend on the size of the area included in the survey We denote the sums of the squares of the differences between the observed and calculated values of N by $v^2(N)$ If r be the probable error of a single observation, the probable errors of N_0, α and β are then determined by

$$0\ 6745\sqrt{\frac{v^2(N)}{m(n-3)}} = m^{-\frac{1}{2}}r,$$

where n denotes the total number of observations and m is a quantity called the "weight" in the theory of probability which has to be determined separately for each of the unknown quantities Calculating the weights by well-known methods, we find, expressing probable errors by square brackets

$$[N_0] = n^{-\frac{1}{2}}r, \qquad [\alpha] = r\sqrt{\frac{B}{AB - C^2}}, \qquad [\beta] = r\sqrt{\frac{A}{AB - C^2}}, \tag{10}$$

with similar expressions for the West Forces It is to be noted that the expressions for the coefficients are considerably simplified if $C = 0$

It is assumed in this investigation that the North and West Forces are independently observed quantities, which in past surveys has not been the case But the probable error being only used to serve as a rough estimate of the extent to which our results may be trusted, there seemed no need to complicate materially the numerical work in order to obtain an improvement of doubtful value

The expression for the probable error of the curl demands attention Equation (9) shows that I depends on a, β and W_0, and as both a and W_0 are derived from the measured West Forces, it is not obvious how the terms should be combined so as to give the probable error of I Sir Frank Dyson, whom I consulted on the matter, was good enough to give me the solution, showing that we may proceed as if we were dealing with three independent variables We therefore find

$$[8I]^2 = 11\ 817\{[a]^2 + [\beta^2]\sec^2\lambda\} + 10^{-6}[W_0]^2\tan^2\lambda \tag{11}$$

The last term is in general negligible

7 We may now proceed to summarise and discuss the results obtained The whole country was divided into nine Districts, but the outbreak of the war prevented the completion of the second District, covering the North-West of Scotland We therefore deal with only eight Districts The geographical outlines of the Districts are shown in fig 1. The figures indicate in terms of γ the values of the North and West Forces at the central point I divided each District further into four quadrants along the lines of latitude and longitude passing through their central point, and I treated each quadrant as a separate unit I was aware that with the reduction in the number of stations less reliance could be placed on the results, but I hoped in this way to find some region comparatively free from disturbance The coefficients for the larger areas were then obtained by intermediate steps, as explained in Article 3

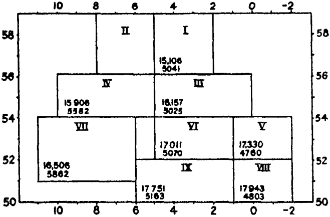

Fig 1

The coefficients, on which the rate of variation of the magnetic forces depend, show considerable irregularities in the smaller sub-divisions of the Districts, and it is not necessary to set them out in detail But it may be useful to give an example of how the calculation was carried out to check, and, if necessary, improve the accuracy of the numerical work, after the coefficients had been obtained as explained in Article 2

I chose for the purpose the West Force in the North-West Quadrant of District VIII, which includes both Greenwich and Kew and contains some anomalous features

Table I —West Force

District VIII, N W Quadrant $a = -0\ 81327 \quad b = +\ 1\ 5004$

Station	$\lambda - \lambda_0$	$l - l_0$	$a(\lambda - \lambda_0)$	$b(l - l_0)$	(C)	(O)	$\iota - (O - C)$	$\iota(\lambda - \lambda_0)$	$\iota(l - l_0)$
Harpenden	+ 15 32	− 5 32	− 12 459	− 7 982	− 20 441	− 19 8	+ 0 641	+ 9 820	− 3 410
Kew	− 4 38	− 7 82	+ 3 562	− 11 733	− 8 171	+ 16 2	+ 24 371	− 106 745	− 190 581
Reading	− 3 48	+ 30 88	+ 2 830	+ 46 332	+ 49 162	+ 1 2	− 47 962	+ 166 908	−1481 066
Windsor	− 3 58	+ 9 18	+ 2 911	+ 13 774	+ 16 685	+ 80 2	+ 63 515	−227 384	+ 583 068
Greenwich	− 3 88	− 26 92	+ 3 155	− 40 390	− 37 235	− 77 8	− 40 565	+ 157 392	+1092 010
Sums	$\delta = 0$	$\epsilon = 0$	− 0 001	+ 0 001	+ 0 001	Zero	Zero	$d = 0\ 009$	$e = +0\ 021$

The meaning of the figures entered in the first four columns of Table I is sufficiently indicated by the headings The columns marked C and O give the calculated and observed values of the West Force diminished by its average value in the quadrant In the last two columns the residuals v are treated in the same way as the originally observed values of the Forces The sums d and e correspond respectively to D and E If the calculation be correct, and λ_0, l_0 are the accurate average values of λ and l, so that δ and ϵ are zero, the sums put down in the bottom row should all be zero, to the degree of the accuracy aimed at An occasional difference of one unit in the last decimal place is, however, unavoidable The finite value of the sum in the last column show that the agreement could be improved by a slight change in the values of a and b The equations of Article 2 yield the corrections, which are

$$\delta a = \frac{\mathrm{B}d - \mathrm{C}e}{\mathrm{AB} - \mathrm{C}^2}, \qquad \delta b = \frac{\mathrm{A}e - \mathrm{C}d}{\mathrm{AB} - \mathrm{C}^2}$$

With the previously calculated values of A, B and C the corrections work out to be -3×10^{-5} and 1×10^{-5} for a and b respectively, and may therefore be looked upon as insignificant If our aim had been only to determine the *differences between the calculated and observed forces*, it would, of course not have been necessary to calculate the value of the forces to more than one decimal place The value of the check, however, repays the additional labour

8 Table II gives the constants obtained in the eight Districts, the upper figures referring to my own results, while the lower ones are those obtained by Mr Walker * Both sets of figures are based on the same observations, and the difference between them is solely due to the substitution of the method of least squares for the approximate method used by Walker In the bottom row, in which all Districts are combined and which therefore applies to the British Isles as a whole, the agreement is remarkable, especially as Mr Walker, in combining the Districts, introduced a conditional equation which eliminates the earth-air current

9. The second and third columns of Table III give the probable errors of the calculated values of N_0 and W_0 as defined by equations (1) From these we obtain the probable errors (r) of a single observation, which are entered in the fourth and fifth columns The figures in brackets again indicate the values derived from Mr Walker's tables, in which the differences between the observed

* In Walker's Tables ('Phil. Trans., vol. 219) there is a misprint on p 32 the West Force at Giggleswick should be 4958 instead of 5958 as printed There is also an insignificant numerical error on p 34, the average latitude in District V should be 52° 45′ 2 instead of 52° 44′ 8.

Table II —Constants for Districts

District	α	β	a	b	θ	ϕ	$\sqrt{\alpha^2+\beta^2}$	$\sqrt{a^2+b^2}$
I	5 634 5 782	1 037 1 433	1 060 1 014	+2 852 +3 037	1 26 13 55	69 36 71 32	5 729 5 956	3 043 3 202
III	6 238 6 295	1 8 1 974	0 776 1 101	+2 334 +2 590	18 50 17 25	71 37 66 58	6 591 6 597	2 459 2 814
IV	6 118 6 114	1 853 2 296	496 1 080	+2 054 +1 968	16 51 20 35	76 25 61 14	6 392 6 531	2 113 2 245
V	6 424 6 592	1 582 1 472	0 132 0 724	+2 755 +2 742	13 56 12 35	8 16 75 13	6 616 6 754	2 758 2 835
VI	6 958 7 303	1 963 1 999	0 173 0 073	+2 656 +2 790	15 45 15 18	8 17 75 20	7 3[illegible] [illegible] 2	2 662 2 791
VII	7 697 7 513	1 7[illegible]8 1 740	0 558 0 537	[illegible] 205 +2 274	12 39 13 2	7 48 76 43	7 888 7 712	2 275 2 337
VIII	8 381 8 309	1 436 1 439	+0 645 +0 722	+2 793 +2 872	9 43 9 51	103 1 104 7	8 504 8 433	2 866 2 961
IX	7 450 7 279	1 533 1 547	0 446 0 493	+2 341 +2 350	11 55 12 0	9 12 78 9	7 614 7 442	2 383 2 400
Whole Area	6 857 6 864	1 608 1 633	0 704 0 726	+2 281 +2 283	13 10 13 23	72 51 72 22	043 7 055	2 387 2 396

Table III —Probable Errors of N_0 W_0 and of Single Observations

Unit of Force = γ

District	N_0	W_0	r (N)	r (W)	(N)	r (W)
I	14 (18)	11 (12)	68 (82)	50 (57)	51	38
III	18 (19	7 (7)	77 (80)	29 (30)	49	25
IV	26 (26)	27 (27)	103 (106)	108 (110)	70	82
V	7 (10)	9 (11)	35 (45)	45 (48)	18	33
VI	8 (9)	7 (9)	37 (47)	36 (44)	18	30
VII	7 (8)	7 (7)	39 (44)	39 (41)	28	29
VIII	4 (8)	9 (10)	19 (33)	37 (44)	18	33
IX	7 (9)	6 (8)	31 (42)	29 (36)	12	23
Average	11 (13)	10 (11)	51 (60)	47 (51)	33	33

and calculated components of force are set out As already stated the error here means the discrepancy between the observed and calculated values and includes not only inaccuracies of measurement but disturbances due to local magnetic causes My calculations were carried out separately for the four quadrants into which each of the Districts was divided and thus furnish a second measure (*r*) of the error of a single observation The average values of these probable errors as derived separately from the four quadrants are entered in the last two columns The comparison between *r* and *r* is significant the former being very consistently nearly 50 per cent greater than the latter both for the West and North Forces This can only be accounted for by the circumstance that the effect of the disturbances in the smaller areas are to a greater extent capable of representation by a linear equation and therefore appear as a change in the coefficients rather than as errors in the sense here used So far as the calculation of the curl is concerned all that matters is that the linear law should hold and it would seem therefore that as a test of the earth air effect a smaller area is preferable With the data at my disposal it was unavoidable that the division of an area into four parts meant a diminution of the observing stations to about five on the average in each quadrant Hence though the probable error of a single observation was diminished that of the coefficients was increased This could be easily amended by increasing the number of stations or the number of observations at each station

10 Table IV gives the current densities of the earth air currents in ampères per square kilometre It will be noticed that the more accurate process of calculation reduces the Districts showing a descending current from two to

Table IV —Earth Air Currents

District	I (A S)	I (C W W)	[I]
I	0 613	− 0 278	0 2 8
III	+ 0 364	+ 0 108	0 235
IV	+ 0 179	+ 0 179	0 830
V	+ 0 285	− 0 048	0 220
VI	+ 0 486	+ 0 555	0 130
VII	+ 0 023	+ 0 040	0 105
VIII	+ 0 514	+ 0 549	0 103
IX	+ 0 084	+ 0 046	0 109

Average (*a*) = + 0 239 ± 0 051 **Average (*b*) = 0 123 ± 0 141**

British Isles, I = 0 0032

one, but the probable errors are too large to allow any certain conclusions to be drawn for the Districts separately We proceed, therefore, to combine them so as to obtain their joint verdict This may be done in several ways The most natural procedure, and probably also the best, is to calculate the general mean in the usual way, the weights of the separate entries being proportional to the inverse squares of the probable errors given in the last column of the table The value obtained in this way is entered as "Average (*a*)," and supplies substantial evidence in favour of the earth-air current, the current density being more than four times as great as the probable error But the argument is considerably weakened if we derive the average curl from the linear formulæ applied to the combined Districts The relevant coefficients are given in the bottom row of Table II With the help of equation (9) we find that the value of I is 0 003, which is practicably negligible Doubts may reasonably be urged with regard to the validity of this method, as it rests on the assumption that the linear formula can be assumed to hold with sufficient accuracy over so large an area as the whole of Great Britain and Ireland The curvature of the lines of force would alone introduce sensible errors

There is a third way of determining the average current density by calculating the total current passing through the whole area, this being equal to the sum of the currents passing through the individual Districts If Q be the area of a District, it follows that the average current over the whole country is $\Sigma(QI)$ divided by ΣQ, and knowing the probable errors of I for the several Districts we may find the probable error of the resulting value If a District cover a range $\Delta\lambda$ and Δl in latitude and longitude, and its mean latitude be λ, the areas are proportional to $\Delta\lambda \, . \, \Delta l \cos\theta$ This procedure leads to the value entered in Table IV as "Average (*b*)" In estimating the value of this procedure, it should be noticed that the probable errors of the District values are not taken account of in this determination of I, but only in the calculation of its probable error The latter is dominated by a great disturbance in District IV, amounting at one station in the North of Ireland to 464γ The accuracy of the method last employed is also affected by an over-estimate of some of the areas It has been assumed for the sake of simplicity that the values of $\Delta\lambda$ and Δl are those laid down by Walker and shown in fig 1 In some Districts, such as VIII, these include appreciable areas covered by sea, where, of course, no observations were taken For this reason it would seem that greater value should be attached to Average (*a*) than to Average (*b*).

In all these calculations the dissenting voice of the first District, covering the North-East of Scotland, is fully taken into account, but its evidence is of doubtful value in consequence of the great disturbances within its precincts Among the 22 stations it contains there are not less than 12 in which the difference between the calculated and observed values exceeds 100γ in one or other of the two components of force At Stirling the difference amounts to 297γ (374γ according to Mr Walker), while at Dundee the discrepancy of 23γ found by Rücker in 1886 has, according to Walker's tables, increased to 207γ, the co-ordinates of the observing stations being changed by about half a mile in latitude and three miles in longitude

11 In comparing our results with those obtained elsewhere I may refer to Dr Adolph Schmidt,* who has recently published the results he derived from charts of Dr Neumayer's survey for 1885 Roughly speaking, they show a belt of inward flow in the equatorial regions not quite parallel to the circles of latitude, but stretching from South-East to North-West The line of zero current separating the two regions cuts through the North-West part of Africa, and thence passes North so that the positive region includes nearly the whole of North America up to a latitude of 60° For Great Britain an outward current of about 0 3 ampère per square kilometre is given, and this is in fair agreement with the weighted mean of the seven Districts of Great Britain found above The same subject has been repeatedly discussed by Dr Bauer,† who dealt with the results derived from more recent charts He gives positive currents from the Poles to latitude 45°, with negative currents farther south If this be correct, we should have to conclude that the line of zero curl passes through North America in higher latitudes than in Western Europe, but not quite so far north as shown in Dr Schmidt's chart

12. In Article 6 it has been shown how the probable errors of the coefficients α and β, which determine the probable error of I, depend on the quantities denoted by A, B, C. In the most favourable case in which the observing stations are placed symmetrically with respect to the central point $C = 0$, and the probable errors for the same value of r are inversely proportional to the square roots of A and B for α and β respectively The definition of these quantities shows that, in order to diminish the effective error, $\Sigma(\lambda - \lambda_0)^2$ and $\Sigma(l - l_0)^2$ should be made as large as possible, which means that for the determination of α the stations should be on the longitude circle and for the determination of β on the latitude circle. It is further to be noticed that a station placed at the central point has no effect whatever on the determination of the coefficients, and hence also takes no part in the calculation of the earth-air current

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* 'Zeitschrift für Geophysik,' vol 1, p. 281 (1925)

† 'Terrestrial Magnetism,' vol 25, p. 151 (1920)

Observations at such stations have their importance in determining the errors, but not in fixing the value of the unknown quantities.

In planning a scheme of operation which may lead to a decisive test of the reality of the curl, we must in the first place form an estimate of the accuracy of our measurements of magnetic force. In the account of their survey of 1886 Rücker and Thorpe give 3γ as the probable error obtained by their observations in the measurement of Horizontal Force with the Kew instrument.* To arrive at this figure two independent observations were taken at a short interval and the error was assumed to be half the difference of the values obtained. But if r be the probable error of one observation, that of half the difference between two observations is $r/\sqrt{2}$. It seems to me, therefore, that their estimate of the probable error should be multiplied by $\sqrt{2}$. The same correction would apply to their second survey,† which gave 5γ for the probable error of an observation. With the instruments at present at our command, the time taken to measure the Horizontal Force is very materially diminished, and we may hope to reduce the probable error substantially. I would propose four stations, two of which are on a meridian circle at a distance $\pm y$ from the central point, and two on a latitude circle at distances $\pm x$ from the same point, the distances being measured in minutes of arc. If we imagine n observations to be taken at each point, or, in other words, n coincident stations to be placed at each of the four points, we find by Articles 2 and 6

$$\mathrm{A} = 2ny^2, \qquad \mathrm{B} = 2nx^2, \qquad \mathrm{C} = 0,$$

$$[\alpha] = \frac{r}{y}\sqrt{\tfrac{1}{2}n}, \qquad [\beta] = \frac{r}{x}\sqrt{\tfrac{1}{2}n},$$

and hence by (11), neglecting the last term

$$[\delta I]^2 = (2n)^{-1}\sigma^2 r^2 (y^{-2} + x^{-2}\sec^2\lambda) \times 10^{-6}$$

If the stations are at the same distance from the central point, we have $y = x\cos\lambda$, and hence, introducing the numerical value of σ,

$$y[\mathrm{I}]\sqrt{n} = 0{\cdot}43r \qquad (12)$$

We are not concerned with the absolute values of the forces and need only consider the accuracy with which the difference between the magnetic forces measured simultaneously in two localities can be determined. We therefore introduce the probable error (r_1) of the difference between two determinations, which is equal to $r\sqrt{2}$. If, as an example, 25 independent measurements are made, equation (12) becomes

$$y[\mathrm{I}] = 0{\cdot}0607r_1.$$

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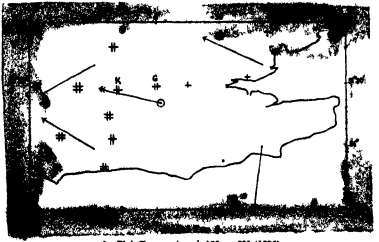
* 'Phil. Trans.,' vol. 181, p. 77 (1890).

† 'Phil. Trans.,' vol. 188, p. 33 (1896).

If we are satisfied with a probable error of I equal to 0 1 and the probable error of a determination of the difference of the forces at two localities can be reduced to 3γ we find for y the value of 1 82 miles The explored area would be a square having for its diagonals a length of 3 6 miles and for its sides a length of 2 6 miles This is the minimum area by means of which we may hope to obtain a decisive result

13 My principal object in undertaking the labour of the detailed calculations of which only a summary is given here was to find an area in which the magnetic forces varied with sufficient regularity Unfortunately my hopes were not fulfilled adjoining parts of a District showing considerable discrepancies

I found however the following relevant statement by Rucker and Thorpe* in their discussion of the magnetic character of the various districts examined by them In Mid Kent and Sussex the horizontal disturbing forces are extraordinarily small being less than the limit of accurate determination of direction at a group of nine neighbouring stations I have not yet been able to identify the stations as the list of 696 included in the survey is arranged in alphabetical order The geographical position indicates however that they must lie in Walker s District VIII This as already mentioned has special interest as it contains Greenwich and Kew and it may be added the new magnetic observatory at Abinger The district as a whole is anomalous it being the only one in which the coefficient a is positive showing an increase of the West Force towards the North Fig 2 is intended to illustrate the main



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* Phil. Trans. A vol. 188, p. 631 (1896)

features of the District It shows the outline of part of the South and East coast, and the observing stations are marked so as to indicate roughly the intensity of the West component For that purpose the stations were divided into four groups in the order of their intensities. The weakest group is indicated by a simple dot, the next by a cross, the third by a horizontal and two vertical lines, while the strongest are marked by two horizontal and two vertical lines The central point is indicated by a ring, Greenwich and Kew by their initials. Looking at that part of the map which lies to the East of Greenwich, we find that, with the exception of Harwich, situated in the top right-hand corner, the increase of force is decidedly towards the North I have entered in the figure the directions of the normal to the lines of equal West Forces both for the four quadrants and the District as a whole, the latter being indicated by a double-headed arrow The coefficients I obtain for the separate quadrants do not indicate any great regularity and show considerable departures from the general average over the whole country. This is not perhaps surprising, the whole District containing only 18 observing stations

14 It is hoped that use may be made of the next sun-spot minimum to put the matter to a test In the meantime there is much to be done in the preliminary work of preparation Apart from the selection of suitable sites, it is necessary to ascertain how far the forces at two stations a few miles apart preserve their relative magnitude, and may be assumed to vary uniformly along the line joining them The unknown quantity here is the possible effect of earth q[illegible] Disturbances either deep-[illegible] high up in the [illegible] likely to vary appreciably in the contemplated areas, but we know very little about [illegible] currents, and their effect may depend on changes in level or geological formations The selection of an instrument suitable for magnetic surveys is also important, and is, I believe, at the present moment engaging the attention of the Ordnance Survey Our problem is somewhat simplified if the method advocated in this paper be adopted, because only four stations are involved, and these may possibly be taken in pairs if the variation be found to be equal at all four stations

The subject is of primary importance to the progress of the science of terrestrial magnetism, and if the deviations from the potential be shown to be [illegible] great as present observations seem to indicate, we cannot altogether exclude the possibility of some unknown cause affecting magnetism in general

An Interpretation of the Spectrum of Ionised Oxygen (O II)

By R H Fowler, F R S and D R Hartree

(Received March 13, 1926)

§1 *Introduction*

The object of this paper is the correlation of the terms of the spectrum of ionised oxygen, deduced by A Fowler[*] from the regularities in the observed spectrum, with the terms to be expected on the theory of complex spectra indicated by Heisenberg,[†] and worked out in some detail by Hund [‡] It will appear that the agreement between observation and theory is most satisfactory A large proportion of the observed terms can be correlated with the theoretical terms almost with certainty All the observed terms can be correlated with theoretical terms in a way which, while less certain, shows regularities which suggest that the correlation is significant Almost all the theoretical terms which would give strong lines in the region searched by A Fowler are represented among the terms already deduced by him

As it is possible to test the theory of Heisenberg and Hund here with far more certainty and completeness than is possible in the Fe-group, where among the theoretical terms there are usually several alternatives with which an observed term might equally well be identified, we have ventured to set out the argument in some detail No test so complete has been possible for an atom homologous with a member of the fifth column of the periodic table (N, P, As, Sb, Bi) previous to the publication of A Fowler's results

§ 2 *Outline of the Heisenberg-Hund Theory of Complex Spectra*

It may be convenient to the reader to begin with a brief sketch of Heisenberg and Hund's theory of complex spectra It must be understood that this contains nothing original and is an outline only By a complex spectrum we mean the spectrum of an atom whose uncompleted n_k groups with $k > 1$ contain more than 1 electron

Altogether there are five numbers which may be used in specifying the orbit of a single electron , those used by Heisenberg and Hund will be written here

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[*] A. Fowler, ' Roy Soc. Proc. ' A, vol. 110, p. 476 (1926)

[†] W. Heisenberg, ' Zeit f. Phys.,' vol 32, p 841 (1925)

[‡] F. Hund, ' Zeit. f Phys ,' vol. 33, p 345 ; vol. 34, p 296 (1925) These papers will be referred to as I and II.

n, k_1, k_2, m_1, m_2 Of these n is the principal quantum number, and retains the same sense as in Bohr's central orbit theory, k_1 is less by $\frac{1}{2}$ than the subsidiary quantum number k of that theory It is usually more convenient to work with k_1 than with k in building up terms of complex spectra, but for the convenience of writing integral suffixes, and on account of its familiarity, it is often convenient to refer to an orbit by its quantum numbers n_k of the central orbit theory $k_2 = k_1 \pm \frac{1}{2}$, when there is only one electron not in a complete group $k_2 = j + \frac{1}{2}$ in the notation adopted here for j (see later), but j is usually interpreted as the angular momentum of the whole atom and so cannot generally be associated with a single electron in an orbit The magnetic energy of the orbit in a weak field is $m_1 g \omega_L h$, where g is given by Lande's "g-formula" and ω_L is a Larmor's rotation frequency, the magnetic energy of an orbit in a strong field is $m_2 \omega_L h$, these define m_1 and m_2 For a single orbit only three of the quantum numbers k_1, k_2, m_1, m_2 are independent

All the electrons in incomplete n_k groups have to be taken into account in working out theoretically what terms are to be expected in a complex spectrum The spectroscopic nature of each term (*i e*, its Zeeman effect and combination rules, which determine whether in the analysis of an observed spectrum the term shall be named an S, P, D   term*) is specified by a quantum number l which relates to the whole set of electrons not in complete groups. It is not necessarily equal to the k_1 of any one of the orbits present, and is taken to be $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$. for S, P, D terms, so that $l = k_1$ when there is only one electron in an incomplete group It may perhaps be thought of as the resultant angular momentum of the incomplete group Each term will also be specified by a certain multiplicity $2r$, and in general will be a multiple term consisting of several members with different values of the "inner quantum number" j†, the j's are uniquely determined by r and l

The relation of the r, l of the terms given by a set of electrons in incomplete groups to the n_k of the separate electrons is worked out as follows The orbit of each n_k electron in a magnetic field is specified by the five quantum numbers n, k_1, k_2, m_1, m_2, the magnetic state of each orbit is given by m_1, m_2, and the magnetic state of a set of electrons is given by $\bar{m}_1 = \Sigma m_1$, $\bar{m}_2 = \Sigma m_2$ Each separate n_k electron can take all its possible magnetic states, subject to the condition that no two electrons can have the same values of all the quantum numbers n, k_1, k_2, m_1, m_2. The separate magnetic states defined by $\bar{m}_1$, $\bar{m}_2$ are then collected up into sets corresponding to the magnetic states of terms of various r, l, j For example, an n_2 orbit ($k_1 = \frac{3}{2}$) has six possible magnetic states, viz —

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* Following Heisenberg and Hund we adopt the notation suggested by Russell and Saunders ('Astrophys Journ,' vol 61, p 64 (1925)), in which the spectroscopic nature of a term is represented by a capital letter and the multiplicity by a small figure written above and to the left

† There are different conventions for the values to be taken for j (only differences are defined by the combination rules); we follow Hund and take $j = 0$ for a singlet s term and $j = \frac{1}{2}$ for a doublet s term, values for all other terms are then given by the possible combinations. For convenience of writing, the separate members of a term in a spectrum of even multiplicity will be indicated by the integral suffixes $j + \frac{1}{2}$. These suffixes agree with those given by Russell and Saunders (*loc. cit.*), and with those used by A. Fowler The number of magnetic terms is $2j + 1$. For a member of a term of even multiplicity this is twice the written value of the suffix.

$$k_1 = \tfrac{3}{2} \left\{ \begin{array}{llllll} k_2 = 1 & & & k_2 = 2 & & \\ m_1 = -\tfrac{1}{2} & \tfrac{1}{2} & & -\tfrac{3}{2} & -\tfrac{1}{2} & \tfrac{1}{2} \quad \tfrac{3}{2} \\ m_2 = -1 & 0 & & -2 & 0 & 1 \quad 2 \end{array} \right.$$

A system formed of an n_2 orbit and an $(n^1)_2$ orbit ($n^1 \neq n$) has 36 magnetic states, since each orbit has six magnetic states and each orbit can take all its magnetic states independently of the other These 36 magnetic states have values of $\bar{m}_1$, $\bar{m}_2$ corresponding to the magnetic states of six terms, viz, ^1S, ^1P, ^1D, ^3S, ^3P, ^3D If the two orbits have the same n, 21 of the 36 magnetic states of the system drop out, some because interchanging the n's of the electrons, leaving the k_1, k_2, m_1, m_2 the same, does not give a different state of the atom when the n's are the same, and some from the condition that no two electrons can have the same k_1, k_2, m_1, m_2 if they have the same n, the magnetic states left have values of m_1, m_2 corresponding to the terms ^1S, ^1D, ^3P

It is not always necessary to go through the calculation of the magnetic states Hund gives a general theoretical rule that if an electron in an n_k orbit is added to an ion in a state specified by values $r = R$, $l = L$ (n, k not being both equal to the n, k of an electron already present) a set of terms is obtained for which l, r are given by $2r = 2R \pm 1$, $|L - k_1| + \frac{1}{2} \leqslant l \leqslant L + k_1 - \frac{1}{2}$ For example, if to an ion with complete 1_1 and 2_1 groups and 2 2_2 orbits, giving a ^3P state* ($2R = 3$, $L = \frac{3}{2}$) a 3_2 electron is added ($k_1 = \frac{3}{2}$), then $2r = 2, 4$, $l = \frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ so that the following states are obtained ^2S, ^2P, ^2D, ^4S, ^4P, ^4D, to find which of these terms persist when the n of the added electron are equal to that of an electron already present, it is necessary to consider the magnetic states of the orbits

Hund also gives an empirical rule that of the terms based on a given state

* This arrangement of electrons also gives a ^1D and a ^1S state.

of the ion and a given n_k orbit of the new electron, those with greater l and greater r usually lie deeper than those of smaller l and r

It is not possible to correlate uniquely the states of an atom with the values of k_2 of the orbits of the individual electrons in incomplete groups, but if the states are due to the addition of an electron to an ion in a state giving a multiple term, the individual members of the resulting multiple terms can be correlated with individual members of the multiple term of the ion from which they were derived This and this only is physically significant, and probably it is only significant when the single electron is in an orbit from which it can be removed much more easily than the electrons in the ion *

In the example given above the correlation is as follows† —

Ion		Atom	
Orbits	Terms	Orbits	Terms
$2_2\,2_2$	$^3P_2$	$2_2\,2_2\,3_3$	$^4D_4\ ^4P_3\ ^4S_2\ ^2D_3\ ^2P_2\ ^2S_1$
	$^3P_1$		$^4D_3\ ^4P_2\ ^4P_1\ ^2D_2\ ^2P_1$
	$^3P_0$		$^4D_1\ ^4D_2$

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* The state of an atom cannot depend on the order in which the electrons filled up the orbits, but when one electron is much more easily removed than any other, it is reasonable to think of it as a "series electron" and the rest of the atom as a "core" consisting of previously captured electrons. On the other hand, when it is almost equally easy to remove an electron from either of two orbits of different n_k, it hardly seems significant to think of either of these electrons as *the* "series electrons", or to correlate the states of the atom to those of the ion left by removal of either electron. *E g*, in Ni I there is a ^3D term due to an electron arrangement with 9 3_3 orbits and 1 4_1 orbit, this can equally well be thought of as due to the addition of a 3_3 orbit to a ^4F state of Ni^+ with 8 3_3 orbits and 1 4_1 orbit, or due to the addition of a 4_1 orbit to a ^2D state of Ni^+ with 9 3_3 orbits, the separate members of the ^3D term of Ni I could be correlated to the members of either the ^4F or ^2D term of Ni II with equal significance

Similarly when an electron is added in an orbit of the same n_k as some orbits already present in the "core", it is sometimes the case that the resulting terms can be correlated equally well with any of several states of the core.

† This table disagrees in one particular with the diagram given by Hund (vol II, p 302) Probably by a misprint, Hund's diagram assigns both members of the ^2D term to the $^3P_1$ state of the ion, and both members of the ^2P term to the $^3P_2$ state of the ion. It can be seen without working out the details that this is incorrect; the number of magnetic terms derived from one term of the ion must be equal to the product of the numbers of magnetic terms for the ion and added electron separately For the 3_3 electron the number of magnetic terms is 6 and for the $^3P_1$ state of the core it is 3, giving a total of 18 magnetic terms based on the $^3P_1$ state of the core. The number of magnetic states of the atom is twice the sum of the suffixes $j + \frac{1}{2}$ of the terms, which is 18 according to the correlation given here, as it should be, but is 22 according to Hund's correlation.

The combination rules are as follows —

(1) Not more than two electrons make transitions from one n_k orbit to another, and then only such transitions take place for which $\Delta k_1 = \pm 1$ for one electron and $\Delta k_1 = 0 \ \pm 2$ for the other (The case when only one electron makes a transition can be thought of as a special case of this when for one electron $\Delta n = \Delta k_1 = 0$)

(2) The terms can be divided into two classes which will be written with and without a bar over the letter (S, P, D) specifying the l value

Within one class $\Delta l = \pm 1$ and occasionally ± 3

Between the two classes $\Delta l = 0$ and occasionally ± 2

It is immaterial which class is indicated by a bar The difference between barred and unbarred terms is just the same as the difference between dashed and undashed terms in the more usual notation but a different notation is perhaps desirable the bar indicating *only* combination properties of the terms while the dash is sometimes taken to indicate something more (*e g*, if the undashed terms fall into a regular Rydberg sequence a double dash is sometimes used for terms which combine like undashed terms of the same l, but do not fall into the same sequence)

(3) $\Delta j = 0 \ \pm 1$

subject to the condition that $j = 0 \rightarrow j = 0$ does not occur

§ 3 *The Spectrum O II*

The normal distribution of electrons of the O^{++} atom among the groups of n_k orbits is presumably

$$O^{++} \qquad 2 \quad 1_1 \ , \ 2 \quad 2_1 \ , \ 2 \quad 2_2$$

giving terms ^3P $^1\overline{D}$, ^1S of which the ^3P may be expected to be the deepest,* then the $^1\overline{D}$, the $^1\overline{D}$ and $^1\overline{S}$ states are metastable

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* The neutral Si atom has two 3_1 orbits in addition to completed groups. Its lowest terms are —

^3P	66370 7	
		77 1
$^3P_1$	66293 6	
		146 1
$^3P_2$	66147 5	
		6075 5
$^1\overline{D}_2$	60072 0	
		9095 5
$^1\overline{S}_0$	50976 5	

The terms are those quoted by Hund (I, p 335) from McLennan and Shaver ('Trans Roy. Soc, Canada,' vol. 18, p 17) adjusted to agree with Fowler's value for $^1\overline{D}_2$ (= 1P, 'Phil, Trans.,' vol. 225, pp 18–19) The next lowest terms are about 25,000

The O^{++} atom has a structure of the same type (2 2_2 orbits in addition to completed groups) so would be expected to have a similar set of deep terms

The spectrum O II of ionised oxygen would therefore be expected to include mainly terms based on a ^3P state of the core, with some based on a $^1\overline{D}$ state and perhaps some based on a $^1\bar{S}$ state

The figure shows the terms to be expected on the theory of Heisenberg and Hund and the observed terms which are correlated with them * The three deep-lying states of O^{++} are indicated by the vertical lines on the right of the diagram (the ^3P state is shown resolved) From these are drawn a series of horizontal lines, which are intersected by a series of vertical lines, and some of the points of intersection are marked with dots Each dot represents a member of a multiple term deduced from the theory of Heisenberg and Hund, those on the same vertical line represent terms due to the same n_k orbit of the "series electron," *i e*, the electron which is additional to the O^{++} core whose states are indicated by the vertical lines on the right, the value of the n_k for the series electron is shown at the top of each line On any one horizontal line the points represent individual members of a multiple term, with the same r, l, j, produced by adding a "series" electron in an orbit of given k but varying n to the O^{++} core in the state represented by the vertical line on the right at which the horizontal line is terminated For example, points on the second and third horizontal lines on the diagram (counting from the top) represent respectively $^3P_2$ and $^3P_1$ terms arising from the addition of a series electron in an n_1 orbit to the O^{++} core in the $^3P_2$, $^3P_1$ states respectively The horizontal lines for the members of a single resultant multiple term are grouped together

When the series electron is in an orbit loosely bound compared to those of the other electrons in incomplete groups, it seems reasonable to expect that the terms due to the addition of orbits of given k but different n to a core in a definite state should form approximately a Rydberg sequence with a limit corresponding to the state of the core, to make the resultant terms comparable it is also necessary that they should be of the same r, k That is, terms represented by points on the same horizontal line on the diagram should form such a sequence, whose limit corresponds to the state of the ion represented by the vertical line on the right at which the horizontal line terminates

The points represent members of multiple terms predicted by the theory of Hund and Heisenberg, the numbers written to the right of the points are the value of the terms given by A. Fowler which are identified with the theoretical

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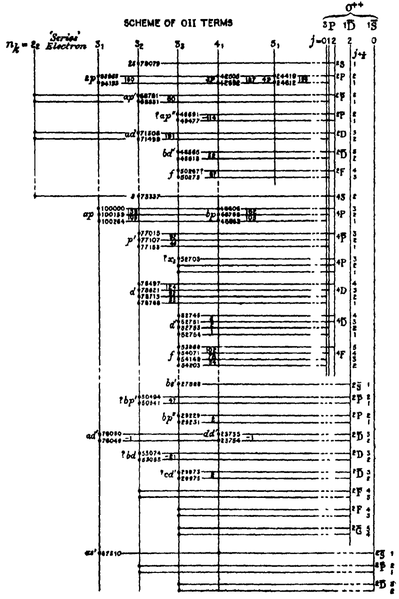
* The idea of this diagram was suggested by the diagram in Hund's second paper.



SCHEME OF OII TERMS

terms, and the separations (in the case of multiple terms)*, on the left are given A Fowler's designations of the terms A query on the left indicates that the identification is considered doubtful, one on the right that the reality of the observed terms is doubtful (usually because only one combination with other terms has been identified among the lines) All A. Fowler's observed terms are represented in the diagram† with one exception, the xd' doublet term 92582, 92533, and A Fowler expresses considerable doubt whether this term is real. The identifications are in some cases fairly certain, in others rather dubious, some of the dubious cases will be mentioned individually later

Hund‡ gives a diagram of the terms due to the addition of a series electron to the ^3P state of the core, but these terms do not seem to account satisfactorily for all those observed for O II, in particular there is no room for s' terms as well as s terms, but terms of both these kinds are certainly observed There are other terms also which can best be accounted for as based on the $^1\bar{D}$ state of the core, and reasons will be given later for thinking this interpretation of these terms is significant

The general agreement between the observed terms and those expected on the theory of Heisenberg and Hund is excellent, except for the doubtful xd' term already referred to, there are no observed terms for which there is no place in the theoretical scheme, and practically all the deeper lying terms which are theoretically to be expected have been observed. Further investigation of the far ultra-violet in the region 400–800 A U will be necessary before much can be said for certain about the deepest-lying $^2\bar{P}$ ^2D and ^4S states Hund's rules that of the terms derived by adding an electron in an orbit of given n_k to a state of the core defined by a given R, L, the term value increases with the r and l of the resultant term, is obeyed in nearly all cases § Only the values of $2s$, ap'' and as' fail to conform to these rules. These rules are not universally obeyed even among the simpler spectra (*e g*, in Ca I the first two ^{1}P terms are less than the corresponding ^{3}P terms, the later ^{1}P terms are greater than the corresponding ^{3}P terms)

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* The lines suggested by A. Fowler as $xd_2' - ad_2$, may be provisionally identified as $ad_{1,2} - f_2$, giving $f_2 = 50273\ 5$, a doublet f term might be expected at just about this value, and the intensities are consistent with this combination; the f_4 member of the term is doubtful, as there are several lines which might be identified as $ad_3 - f_4$ This f_2 term and a possible f_4 term are given on the diagram

† A. Fowler's apparently single term s_2 which combines with the quartet terms s, p', d has been provisionally identified as the unresolved first p'' term of the quartet system.

‡ *Loc. cit.*, II, p. 302.

§ The term values for the doublet terms are based on a series limit calculated from $2p_2$, $3p_2$, $4p_2$; those for the quartet terms are based on an assumed value for ap_2, which, however, does not seem likely to be in error by more than 3000 The zero of term value is the state of the atom in which the core is in the $^3P_2$ state and the "series" electron is at rest at infinity.

There seem to be the beginnings of three sequences of Rydberg type among the observed terms The most definite is the ^{2}P sequence arising from the addition of n_1 orbits to the ^{3}P state of the core, each of these ^{2}P terms consist of two members, one based on the ^{3}P$_1$ state and the other on the ^{3}P$_2$ state of the core The added orbit, having $k = 1$, is not likely to affect the separation much, so it would be expected that the separations of the doublets would all be about the same, and would tend to the difference between the ^{3}P$_1$ and ^{3}P$_2$ states of the core as the principal quantum number of the orbit of the series electron increased This is the case, the three observed ^{2}P terms have separations 180, 187, and 193, while the ^{3}P state of the core probably has separations about 107, 204,* of which the latter is the difference between the ^{3}P$_1$ and ^{3}P$_2$ states The signs of the differences in the O II spectrum agree with what would be expected from the sign of the differences in the O III term †

The quartet terms *ap*, *bp* probably also form the beginning of a sequence of Rydberg type The separations of the terms would be expected to tend to the separations 107, 204 of the ^{3}P state of the core as the principal quantum number *n* of the orbit of the series electron increases, but when *n* is small they would be expected to agree more nearly with the ratio 3 5 given by Landé's interval rule for quartet terms The separations for the two observed terms are 105, 158 and 105, 161, the smaller separation 105 agrees well with the corresponding separation of the core terms, the separations 158, 161 are smaller even than is required by the interval rule

The identification of the observed *ad'*, *dd'* terms as the first two terms of a Rydberg sequence due to adding n_1 orbits to the $^1\bar{\text{D}}$ state of the core, seems at first sight much less certain than the identification of the terms of the ^{2}P and ^{4}P sequences, but the following three points suggest that it may be correct, though the combined evidence is not conclusive

(1) If the terms are taken as members of a sequence of Rydberg type we find -22000 for the limit of the sequence, which would indicate that the $^1\bar{\text{D}}$ term of O III is about 22000 less than the ^{3}P term The O III spectrum is not known well enough to check this value, but it seems very reasonable, for the Si I

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* Millikan and Bowen's triplet with these separations at λ 703 is provisionally identified as a triplet of O III involving the ^{3}P states.

† By definition, a separation of members of a multiple term is reckoned positive when the deeper-lying member has the smaller *j*

spectrum (which has the same general structure as O III) the corresponding difference is 6000 ; it would be expected to increase with core charge (perhaps more rapidly than the first power but less rapidly than the second) and from one row of the periodic table to the next

(2) It would be expected that terms due to adding a series electron in a given n_k orbit to the $^1\bar{D}$ state of the core would differ from those due to adding a series electron in the same orbit to the ^3P state of the core by roughly the difference of term values for the two core states, and actually the difference between such corresponding terms is about 22000 in all cases

(3) Small separations would be expected for terms due to adding an n_1 orbit to a singlet state of the core , the actual doublet separations of the *ad'*, *dd'* terms are both −1

The values of the terms due to adding a 3_3 orbit to the various states of the core are interesting The term value for a 3_3 orbit in the field of a point charge 2 is $\frac{4}{9}R = 48772$, if in O^+ the 3_3 orbit lies entirely outside the core, as would be expected from a consideration of orbital dimensions, the terms due to addition of it to the core would be expected to have about this value (reckoned from the appropriate state of the core) It is actually the case that the observed terms identified as due to the addition of a 3_3 orbit to the core have values close to 48772 (on the whole rather greater, as might perhaps be expected from analogy with simpler spectra) Further, the separations of the doublets (*bp'*, *ad'*) due to adding the 3_3 orbit to the $^1\bar{D}$ state of the core are both small (about 2 in each case) as might perhaps be expected, for (speaking roughly) the external 3_3 orbit itself is not likely to contribute much to the separation, and the core, being in a singlet state, has no separation which the added orbit might affect *

In this row of the periodic table the deepest lying terms are due to adding an electron in a 2_2 orbit to the two already existing in the core , the terms next in order of magnitude may be expected to be those due to the series electron in orbits of quantum number 3_1, 3_2 and 3_3, in this order, as is the case In the next row of the periodic table after the normal 3_2 orbit the first orbits of the series electron with $k = 1, 2, 3$ will be 4_1, 4_2 and 3_3 respectively , the terms due to the 3_3 orbits of the series electron are quite likely to lie deeper than those due to the 4_2 orbit, and perhaps deeper than those based on the 4_1 orbit Hund's diagram is drawn for the case in which the first set of terms due to an n_3 orbit of the series electron lie between the first set due to an n_1 orbit and the first set, after the deepest lying $^4S\ ^2\bar{P}\ ^2D$ terms, due to an n_3 orbit, this may be the case for elements in later rows of the periodic table, when the principal quantum number for the first n_3 orbit is different from that for the first n_1 and n_2 orbits (apart from the normal orbit), but it would not be expected to be the case for N I, O II, etc A similar difference is to be expected between other spectra of the elements of the first row of the periodic table and those of corresponding elements of later rows, *e g*, in Si I the terms due to the 3_3 orbit of the series electron lie between those due to the 4_1 and 4_2 orbits, while for C I it would be expected that the terms due to the 3_1 and 3_2 orbits of the series electron would lie deeper than those due to the 3_3 orbit

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* When the core is not in a state giving a singlet term, the addition of a series electron even in an external orbit (with $k = 1$) may effect the separations considerably, *cf* Heisenberg's formula for separations of terms due to 2 orbits not in complete groups (*loc. cit.*, p. 853).

The term *as′* (87310) only appears in one pair, and A Fowler appears to consider its reality somewhat doubtful It is the only observed term which it seems necessary to consider as based on the $^1\bar{S}$ state of the core As such its value is not altogether satisfactory, from the estimated value 22000 for the wave number difference between the ^3P and $^1\bar{D}$ states of the core, and analogy with Si I, $^1\bar{S}$ for the core would be expected to lie less deep than ^3P by about 55000, so the $^2\bar{S}$ term, due to addition of a 3_1 orbit to the $^1\bar{S}$ state of the core, might be expected to lie between 40000 and 50000, instead of at 87310

The terms *bp′*, *bs′*, *cd′* might be identified as terms based on the $^1\bar{S}$ state of the core, but in view of the close agreement in term value between *bp′* and *bd′*, and between *bs′*, *bp″*, *cd′* the identification adopted appears more probable

The definite absence of the combination *ad* − *ap″*, and the large negative separation of the term *ap″* throws doubt on the identification of this term, but there seems little prospect of explaining it in any other way on the theory of Heisenberg and Hund There is always the possibility that terms based on other states of O III might occur, the deepest would be a $^2\bar{P}$ term due to the electron arrangement 2_2, 3_1, 3_1 (in addition to the electrons in completed 1_1 and 2_1 groups), and the next a group of terms (including a ^2P term) due to the arrangement 2_2, 3_1, 3_2, but these terms would be expected to be very much smaller than the observed *ap″* terms

An interesting combination appears in the quartet system, viz, $s - d'$ This has $\Delta l = 2$ but $\Delta k = 1$ for the series electron and $\Delta k = 0$ for the other electrons, in conformity with Heisenberg's combination rules

Among Millikan and Bowen's lines in the far ultra-violet there is no triplet recorded with separations 158, 105 which might be identified as the resonance triplet $^4S - {}^4P$ of the quartet system, there is a pair of lines with separation 180, which is equal to the separation of the $2p$ term, and which may be the intercombination resonance doublet $^4S - {}^2P$ (as suggested by Fowler), but this seems rather unlikely as the resonance triplet $^4S - ^4P$ would be expected to be stronger than such an intercombination doublet, and no other intercombination lines have so far been recognised *

On the theory of Heisenberg and Hund, however, the normal state of the O^+ atom must give a quartet term, in order that the addition of a further electron should give the triplets and quintets† of the observed O I spectrum Further, the normal state of O^+ probably gives an S term, because the addition of a further electron to an ion in any but an S state does not usually give such well developed sequences of the Rydberg type as those observed for O I ‡ Thus from consideration of the spectrum O I it is possible to say that the deepest term of the O II spectrum is probably a ^4S term

§ 4 *Summary*

The terms of the O II spectrum deduced from the observed lines by A. Fowler are correlated with theoretical terms expected on the theory of complex spectra recently developed by Heisenberg and Hund Some of the identifications cannot be made with certainty but the general agreement between observation and theory is satisfactory

No lines involving the deepest-lying terms have yet been identified, but from consideration of the O I spectrum it appears likely that the normal term of the O II spectrum is a quartet S term

In conclusion we wish to express our thanks to Prof A Fowler, F R S, for putting at our disposal his experimental results before publication

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* In the case of Si I intercombinations between the singlet and triplet systems involving the deepest lying terms do occur, but are not as strong as combinations within the singlet or triplet systems of terms.

† See A Sommerfeld, 'Atombau und Spectrallinien,' 4th Ed., p. 598.

‡ The normal electron arrangement of the neutral O atom gives a ^1D and a ^1S state as well as the ^3P state identified by Hopfield; these singlet states have not yet been identified experimentally

The Relativity Theory of Plane Waves.

By O R Baldwin and G B Jeffery.

(Communicated by Prof L N G Filon, F R S --Received January 15, 1926)

Weyl* has shown that any gravitational wave of small amplitude may be regarded as the result of the superposition of waves of three types, viz (i) longitudinal-longitudinal, (ii) longitudinal-transverse, (iii) transverse-transverse Eddington† carried the matter much further by showing that waves of the first two types are spurious, they are "merely sinuosities in the co-ordinate system," and they disappear on the adoption of an appropriate co-ordinate system The only physically significant waves are transverse-transverse waves, and these are propagated with the velocity of light He further considers electromagnetic waves and identifies light with a particular type of transverse-transverse wave There is, however, a difficulty about the solution as left by Eddington In its gravitational aspect light is not periodic The gravitational potentials contain, in addition to periodic terms, an aperiodic term which increases without limit and which seems to indicate that light cannot be propagated indefinitely either in space or time This is, of course, explained by noting that the propagation of light implies a transfer of energy, and that the consequent change in the distribution of energy will be reflected in a cumulative change in the gravitational field But, if light cannot be propagated indefinitely, the fact itself is important, whatever be its explanation, for the propagation of light over very great distances is one of the primary facts which the relativity theory or any like theory must meet

In endeavouring to throw further light on this question, it seemed desirable to avoid the assumption that the amplitudes of the waves are small, terms neglected on this ground might well have a cumulative effect All the solutions discussed in this paper are exact

When the amplitudes are not small it is no longer true that any wave may be resolved into waves of Weyl's three types We may nevertheless discuss these types as important particular cases In the earlier part of this paper we show that Eddington's results are still true for waves of finite amplitude, longitudinal-longitudinal and longitudinal-transverse waves are spurious, and transverse-transverse waves are propagated with the velocity of light

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* 'Raum, Zeit, Materie,' 4th edition, p. 228, English edition, p 252

† 'Roy Soc. Proc.,' A, vol 102, p 268 (1922)

In § 5 the theory of the propagation of plane transverse-transverse waves is shown to depend on the solution of a single differential equation with five dependent variables Since we deal only with particular solutions, it is not possible to state the result with certainty, but a strong presumption is created that an infinite plane electromagnetic wave (or pulse) cannot be propagated without change of the wave-form There is little doubt but that this result arises from the infinite character of the wave-front, and it seems that the fuller working out of the relativity theory of light must come through the study of divergent waves

§ 2 *The Field Equations*

The equations to be satisfied in space devoid of matter and charge are

(1)
$$G_{\mu\nu} = -8\pi\gamma E_{\mu\nu},$$

where $G_{\mu\nu}$ is the contracted Riemann-Christoffel tensor, γ is the constant of gravitation, and $E_{\mu\nu}$ is the electromagnetic energy tensor, together with the electromagnetic equations

(2)
$$\frac{\partial}{\partial x_\nu}\left\{F^{\mu\nu}\sqrt{(-g)}\right\} = 0,$$

where $F^{\mu\nu}$ is the electromagnetic force tensor

If $B_{\mu\nu\sigma}{}^{\lambda}$ is the Riemann-Christoffel tensor, we have

(3)
$$g_{\rho\alpha}B_{\mu\nu\sigma}{}^{\alpha} = B_{\mu\nu\sigma\rho} = (\mu\rho\sigma\nu)$$

and

(4)
$$G_{\mu\nu} = B_{\mu\nu\alpha}{}^{\alpha} = g^{\rho\sigma}(\mu\rho\sigma\nu).$$

The Christoffel four-index symbols are given by

(5)
$$(\mu\rho\sigma\nu) = \tfrac{1}{2}\left\{\frac{\partial^2 g_{\mu\nu}}{\partial x_\rho \partial x_\sigma} + \frac{\partial^2 g_{\rho\sigma}}{\partial x_\mu \partial x_\nu} - \frac{\partial^2 g_{\mu\sigma}}{\partial x_\rho \partial x_\nu} - \frac{\partial^2 g_{\rho\nu}}{\partial x_\mu \partial x_\sigma}\right\}$$
$$- g^{\alpha\beta}[\mu\sigma, \alpha][\rho\nu, \beta] + g^{\alpha\beta}[\mu\nu, \alpha][\rho\sigma, \beta],$$

in which the Christoffel three-index symbols of the first kind are given by

(6)
$$[\mu\sigma, \alpha] = \tfrac{1}{2}\left(\frac{\partial g_{\mu\alpha}}{\partial x_\sigma} + \frac{\partial g_{\sigma\alpha}}{\partial x_\mu} - \frac{\partial g_{\mu\sigma}}{\partial x_\alpha}\right)$$

If κ_μ is the electromagnetic potential vector

(7)
$$F_{\mu\nu} = \frac{\partial\kappa_\mu}{\partial x_\nu} - \frac{\partial\kappa_\nu}{\partial x_\mu},$$

and the electromagnetic energy tensor is defined by

(8)
$$E_\mu{}^\nu = -F_{\mu\alpha}F^{\nu\alpha} + \tfrac{1}{4}g_\mu{}^\nu F_{\alpha\beta}F^{\alpha\beta}$$

For plane waves propagated with velocity V in the negative direction of x_1 we assume that the components of all tensors are functions only of $\xi \equiv x_1 + Vx_4$. The electromagnetic equations (2) then give three independent equations which at once integrate to show that

$$(F^{14},\ F^{21} + VF^{24},\ F^{31} + VF^{34})\sqrt{(-g)}$$

are constants. These are components of a tensor density defining the force per unit mesh on charge moving with velocity V with the waves. By the superposition of an appropriate static homogeneous field these constants can be made to be zero.*

We accordingly take

(9) $$F^{14} = 0$$

(10) $$F^{21} + VF^{24} = 0$$

(11) $$F^{31} + VF^{34} = 0$$

Denoting differentiations with respect to ξ by accents and writing

(12) $$\kappa_4 = V\kappa_1 = \kappa_0$$

we have

(13) $$F_{\mu\nu} = \begin{array}{c|cccc} & \xrightarrow{\mu} & & & \\ \downarrow \nu & 0 & \kappa_2 & \kappa_3 & \kappa \\ & \kappa_2 & 0 & 0 & V\kappa_2 \\ & -\kappa_3 & 0 & 0 & V\kappa_3 \\ & \kappa & V\kappa_2 & V\kappa_3 & 0 \end{array}$$

Using these values we have

$$\tfrac{1}{2} F_{\alpha\beta} F^{\alpha\beta} = \kappa_0 F^{41} + \kappa_2 \{F^{21} + VF^{24}\} + \kappa_3 \{F^{31} + VF^{34}\}$$
$$= 0$$

by (9)–(11). Hence (8) reduces to

(14) $$E_\mu^{\ \nu} = F_{\mu\alpha}F^{\nu\alpha}$$

§ 3 *Longitudinal Longitudinal Waves*

For these waves

(15) $$g_{\mu\nu} = \begin{array}{cccc} g_{11} & 0 & 0 & g_{14} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ g_{14} & 0 & 0 & g_{44} \end{array}$$

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* A similar situation arises in the ordinary wave theory of light when the integration of Maxwell's equations gives in the first instance that E_x, $H_z + VE_y$, $H_y - VE_z$, are constants. These are taken as zero for ordinary light; non zero values of the constants arising in the theory of the Zeeman and Stark effects.

The determinant of $g_{\mu\nu}$,

(16)
$$g = g_{11}g_{44} - g_{14}^2,$$

and

(17)
$$gg^{\mu\nu} = \begin{matrix} g_{44}, & 0, & 0 & -g_{14} \\ 0, & -g & 0, & 0 \\ 0, & 0, & -g, & 0 \\ -g_{14}, & 0, & 0, & g_{11} \end{matrix}$$

The three index symbols of the first kind vanish unless each index is either 1 or 4, and

(18)
$$[11, 4] = g_{14}' - \tfrac{1}{2}Vg_{11}', \qquad [44, 1] = Vg_{14}' - \tfrac{1}{2}g_{44}',$$
$$[14, 1] = V[11, 1] = \tfrac{1}{2}Vg_{11}',$$
$$[44, 4] = V(14, 4] = \tfrac{1}{2}Vg_{44}'$$

From (5) we see that the four index symbols vanish unless each index is either 1 or 4, and owing to their anti-symmetry, the only independent surviving symbol is

(19)
$$(1414) = -\tfrac{1}{2}\sqrt{(-g)}\frac{d}{d\xi}\left\{\frac{1}{\sqrt{(-g)}}\frac{d}{d\xi}(V^2g_{11} - 2Vg_{14} + g_{44})\right\}$$

From (4) we have

(20)
$$G_{11} = -g^{44}(1414),\ G_{14} = g^{14}(1414),\ G_{44} = -g^{11}(1414)$$

the remaining components of $G_{\mu\nu}$ vanishing

From (13) and (17) we obtain

(21)
$$g\,F^{\mu\nu} = \begin{matrix} 0, & -(g_{44}-Vg_{14})\kappa_2', & -(g_{44}-Vg_{14})\kappa_3', & \kappa_0' \\ (g_{44}-Vg_{14})\kappa_2', & 0, & 0, & -(g_{14}-Vg_{11})\kappa_2' \\ (g_{44}-Vg_{14})\kappa_3', & 0, & 0, & -(g_{14}-Vg_{11})\kappa_3' \\ -\kappa_0', & (g_{14}-Vg_{11})\kappa_2', & (g_{14}-Vg_{11})\kappa_3', & 0. \end{matrix}$$

$$\begin{array}{l} \xrightarrow{\ \mu\ } \\ \big\downarrow \nu \end{array}$$

Substituting these values in (9)–(11), we have either (i) $\kappa_0' = \kappa_2' = \kappa_3' = 0$, or (ii) $\kappa_0' = 0$ and $g_{44} - 2Vg_{14} + V^2g_{11} = 0$ In the first case $E_{\mu\nu} = 0$, and therefore $G_{\mu\nu} = 0$ Hence from (20), $(1414) = 0$ In the second case $(1414) = 0$ by (19) It follows that for any longitudinal-longitudinal wave all the components of the Riemann-Christoffel tensor vanish. Accordingly, such waves are spurious in the sense that they disappear on the application of an appropriate transformation of co-ordinates.

§ 4 *Longitudinal Transverse Waves*

In this case

$$(22)\qquad g_{\mu\nu} = \begin{matrix} -1 & g_{12} & g_{13} & 0 \\ g_{12} & -1 & 0 & g_{24} \\ g_{13} & 0 & -1 & g_{34} \\ 0 & g_{24} & g_{34} & 1 \end{matrix}$$

The contravariant $g^{\mu\nu}$ the 3 index symbols and the 4 index symbols are more complicated than in the last case and it is convenient to proceed somewhat differently From (8) we have

$$\begin{aligned} F_{2\nu} &= - F_{2\alpha}F^{\nu\alpha} = - F_{21}F^{\nu 1} - F_{24}F^{\nu 4} \\ &\quad - \kappa_2 (F^{\nu 1} + VF^{\nu 4}) \\ &\quad 0 \end{aligned}$$

for ν 1 2 3 4 by (9) (11) Similarly $E_{3\nu} = 0$ It follows that

$$(23)\qquad F_{2\nu} \quad 0 \qquad E_{3\nu} - 0$$

and the only non vanishing components of $\Gamma_{\mu\nu}$ are E_{11} F_{14} E_{44}

Hence from (1) we have in particular

$$(24)\qquad G_{22} \quad 0 \qquad G_{33} - 0$$

We will first calculate the 4 index symbols necessary to determine G_{22} and G_{33} viz $(2\rho\sigma\ 2)$ and $(3\rho\sigma\ 3)$ The non vanishing 3 index symbols are

$$\begin{aligned} (25)\qquad &[11\ 2] - g_{12} \quad [11\ 3] \quad g_{13} \quad [44\ 2] \quad Vg_{24} \quad [44\ 3] - Vg_{34} \\ &[14\ 2] \quad \tfrac{1}{2}(g_{24} \quad Vg_{12}) \quad [14\ 3] \quad \tfrac{1}{2}(g_{34} + Vg_{13}) \\ &[12\ 4] \qquad [24\ 1] \quad \tfrac{1}{2}(g_{24} \quad Vg_{12}) \\ &[13\ 4] - \qquad [34\ 1] \quad \tfrac{1}{2}(g_{34} \quad Vg_{13}) \end{aligned}$$

From these we obtain

$$\begin{aligned} (26)\qquad &\frac{(2112)}{g^{44}} = -\frac{(2142)}{g^{14}} - \frac{(2442)}{g^{11}} = -\tfrac{1}{4}(g_{24} - Vg_{12})^2 \\ &\frac{(3113)}{g^{44}} - -\frac{(3143)}{g^{14}} - \frac{(3443)}{g^{11}} = -\tfrac{1}{4}(g_{34} - Vg_{13})^2 \end{aligned}$$

all other symbols of the type $(2\rho\sigma\ 2)$ $(3\rho\sigma\ 3)$ vanishing

Hence

$$\begin{aligned} (27)\qquad G_{22} &- -\tfrac{1}{4}\{g^{11}g^{44} - (g^{14})^2\}\{g_{24} - Vg_{12}\}^2 \\ G_{33} &\quad \tfrac{1}{4}\{g^{11}g^{44} \quad (g^{14})^2\}\{g_{34} \quad Vg_{13}\}^2 \end{aligned}$$

Now
$$g^{11} g^{44} - (g^{14})^2 = \begin{vmatrix} g^{11} & g^{12} & g^{13} & g^{14} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ g^{14} & g^{24} & g^{34} & g^{44} \end{vmatrix}$$

Multiplying by the determinant g we obtain $g^{11} g^{44} \quad (g^{14})^2 \quad 1/g$ and therefore can never be zero Accordingly from (27) we must have

(28)
$$g_{24} \quad Vg_{12} - 0 \qquad g_{34} \quad Vg_{13} \quad 0$$

If these are satisfied all the 3 index symbols vanish except

(29)
$$\begin{array}{lll} [11\ 2] - g_{12} & [14\ 2] \quad g_{24} & [44\ 2] - Vg_{24} \\ [11\ 3] - g_{13} & [14\ 3] \quad g_{34} & [44\ 3] - Vg_{34} \end{array}$$

It may now be shown that all the 4 index symbols vanish In (5) the terms involving the second differential coefficients will vanish unless of the four indices one is 2 or 3 and the remaining three are 1 or 4 It is easily verified that in this case these terms vanish by reason of (28) The terms involving the 3 index symbols will vanish unless all four indices are 1 or 4 Hence the only possible surviving symbol is

$$\begin{aligned} (1414) \qquad & g^{\alpha\beta} [11\ \alpha] [44\ \beta] + g^{\alpha\beta} [14\ \alpha] [14\ \beta] \\ & = (g^{22} g_{24} + g^{23} g_{34})(g_{24} - Vg_{12}) + (g^{23} g_{24} + g^{33} g_{34})(g_{34} - Vg_{13}) \\ & = 0 \end{aligned}$$

by (28)

Hence for any longitudinal transverse wave all components of the Riemann Christoffel tensor vanish the wave is spurious and may be transformed away by an appropriate change of co ordinates

§ 5 *Transverse Transverse Waves*

For these waves

(30)
$$g_{\mu\nu} - \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & g_{22} & g_{23} & 0 \\ 0 & g_{23} & g_{33} & 0 \\ 0 & 0, & 0 & 1 \end{array}$$

The determinant of $g_{\mu\nu}$ is

(31)
$$g = g_{23}^2 - g_{22} g_{33}$$

and

(32)
$$g\, g^{\mu\nu} = \begin{array}{cccc} -g & 0 & 0 & 0 \\ 0 & -g_{33} & g_{23} & 0 \\ 0 & g_{23} & -g_{22} & 0 \\ 0 & 0 & 0, & g \end{array}$$

The 3 index symbols vanish unless one index is 1 or 4 and the other two 2 or 3 We find

$$(33)\qquad V[12\ 2] \qquad V[22\ 1] - \quad [22\ 4] \quad [24\ 2] - \tfrac{1}{2} Vg_{22}$$
$$V[12\ 3] - V[13\ 2] \qquad V[23\ 1] = \quad [23\ 4]$$
$$[24\ 3] \quad [34\ 2] = \tfrac{1}{2} Vg_{23}$$
$$V[13\ 3] \qquad V[33\ 1] = -[33\ 4] = [34\ 3] = \tfrac{1}{2} Vg_{33}$$

The eleven 4 index symbols which do not vanish identically are

$$(34)\quad (1212) = -\tfrac{1}{2} g_{22}'' + \tfrac{1}{4}\{g^{22}g_{22}'^{2} + 2g^{23}g_{22}' g_{23}' + g^{33}g_{23}'^{2}\}$$
$$(1213) \quad -\tfrac{1}{2} g_{23}'' + \tfrac{1}{4}\{g^{22}g_{22}' g_{23}' + g^{23}(g_{22}' g_{33}' + g_{23}'^{2}) + g^{33} g_{23}' g_{33}'\}$$
$$(1313) - -\tfrac{1}{2} g_{33}'' + \tfrac{1}{4}\{g^{22}g_{23}'^{2} + 2g^{23}g_{23}' g_{33}' + g^{33}g_{33}'^{2}\}$$
$$(4242) \quad V(1242) \quad V^{2}(1212)$$
$$(4343) \quad V(1343) \quad V^{2}(1313)$$
$$(4243) \quad V(1243) \quad V(4213) \quad V^{2}(1213)$$
$$(2323) - \tfrac{1}{4}(1 \quad V^{2})(g_{22}' g_{33}' \quad g_{23}'^{2})$$

From these values and (4) we have

$$(35)\qquad G_{11} \quad - g^{22}(1212) \quad 2g^{23}(1213) - g^{33}(1313)$$
$$(36)\qquad G_{44} - V G_{14} \quad V^{2} G_{11}$$
$$(37)\qquad G_{22} - (1 \quad V^{2})\{(1212) - \tfrac{1}{4} g^{33}\, g_{22}' g_{33}' - g_{23}'^{2})\}$$
$$(38)\qquad G_{23} \quad (1 \quad V^{2})\{(1213) + \tfrac{1}{4} g^{23}(g_{22}' g_{33}' - g_{23}'^{2})\}$$
$$(39)\qquad G_{33} - (1 - V^{2})\{(1313) - \tfrac{1}{4} g^{22}(g_{22}' g_{33}' - g_{23}'^{2})\}$$

For purely gravitational waves $G_{\mu\nu} - 0$ If $V^{2} \neq 1$ we have from (37)–(39)

$$(40)\qquad (1212) \quad \tfrac{1}{4} g^{33}(g_{22}' g_{33}' - g_{23}'^{2})$$
$$(1213) \quad -\tfrac{1}{4} g^{23}(g_{22}' g_{33}' \quad g_{23}'^{2})$$
$$(1313) \quad \tfrac{1}{4} g^{22}(g_{22}' g_{33}' - g_{23}'^{2})$$

Substituting in (35) we have

$$\{g^{22} g^{33} - (g^{23})^{2}\}(g_{22}' g_{33}' - g_{23}'^{2})$$
$$= -(g_{22}' g_{33}' - g_{23}'^{2})/g - 0$$

Hence from (37)–(39) (1212) – (1213) = (1313) – 0 and we see from (34) that all components of (μρσν) vanish and hence the Riemann Christoffel tensor vanishes Purely gravitational waves are spurious unless the velocity of propagation is unity, in which case the equations $G_{\mu\nu} = 0$ reduce to the single equation $G_{11} = 0$

Passing to the case of electromagnetic waves, we have from (13) and (32)

$$(41) \quad gF^{\mu\nu} = \begin{array}{l} \xrightarrow{\quad} \mu \\ \Big\downarrow \\ \nu \end{array} \begin{array}{cccc} 0 & g_{33}\kappa_2' - g_{23}\kappa_3', & -(g_{23}\kappa_2' - g_{22}\kappa_3'), & -g\kappa_0' \\ -(g_{33}\kappa_2' - g_{23}\kappa_3'), & 0, & 0, & V(g_{33}\kappa_2' - g_{23}\kappa_3'). \\ g_{23}\kappa_2' - g_{22}\kappa_3', & 0 & 0, & V(g_{23}\kappa_2' - g_{22}\kappa_3') \\ g\kappa_0', & -V(g_{33}\kappa_2' - g_{23}\kappa_3), & V(g_{23}\kappa_2' - g_{22}\kappa_3') & 0 \end{array}$$

From (9)–(11) we have $\kappa_0 = 0$ and

$$(1 - V^2)(g_{33}\kappa_2' - g_{23}\kappa_3') = 0$$

$$(1 - V^2)(g_{23}\kappa_2' - g_{22}\kappa_3') = 0$$

If $V^2 \neq 1$, these give $\kappa_2' = \kappa_3 = 0$, since $g_{23}^2 - g_{22}g_{33} = g \neq 0$, we are led back to the purely gravitational waves already discussed Hence for electromagnetic waves, the velocity of propagation is unity and $\kappa_0' = 0$ Making this simplification and calculating $E_{\mu\nu}$ from (13), (14) and (41) we find

$$(42) \quad E_{11} = E_{14} = E_{44}$$

$$= (g_{33}\kappa_2'^2 - 2g_{23}\kappa_2'\kappa_3' + g_{22}\kappa_3'^2)/g,$$

the remaining components vanishing Thus, in view of (35)-(39), the equations (1) reduce to the single equation $G_{11} = -8\pi\gamma E_{11}$ that is to

$$(43) \quad g_{33}g_{22}'' - 2g_{23}g_{23}'' + g_{22}g_{33}''$$

$$+ \frac{1}{2g}\Big[g_{33}\{g_{33}g_{22}'^2 - 2g_{23}g_{22}'g_{23}' + g_{22}g_{23}'^2\}$$

$$-2g_{23}\{g_{33}g_{22}'g_{23}' - g_{23}(g_{22}'g_{33}' + g_{23}'^2) + g_{22}g_{23}'g_{33}'\}$$

$$+ g_{22}\{g_{33}g_{23}'^2 - 2g_{23}g_{23}'g_{33}' + g_{22}g_{33}'^2\}\Big]$$

$$= 16\pi\gamma(g_{33}\kappa_2'^2 - 2g_{23}\kappa_2'\kappa_3' + g_{22}\kappa_3'^2)$$

which may be written more concisely as

$$(44) \quad g_{33}g_{22}'' - 2g_{23}g_{23}'' + g_{22}g_{33}'' - g\frac{d^2}{d\xi^2}(\log g)$$

$$= 32\pi\gamma(g_{33}\kappa_2'^2 - 2g_{23}\kappa_2'\kappa_3' + g_{22}\kappa_3'^2)$$

This differential equation represents the only condition imposed by th general relativity theory on the five variables $g_{22}, g_{23}, g_{33}, \kappa_2, \kappa_3$ for the propagation of plane waves It possesses a variety of simply periodic solutions in which the variables differ from constant mean values by terms of the type A cos $p\xi$ + B sin $p\xi$ where A and B are different for the different variables But these solutions have no physical significance since in every case they imply the periodic vanishing of the determinant g

If the $g_{\mu\nu}$ differ from their Galilean values by small quantities the squares of which may be neglected equation (44) becomes

$$g_{22}'' + g_{33}'' = 16\pi\gamma(\kappa_2^2 + \kappa_3^2) \tag{45}$$

which agrees with the equation given by Eddington who discusses the particular solutions in which $g_{22} + g_{33} = \text{const}$ (purely gravitational waves) and $g_{22} = g_{33}$ (light waves) The corresponding exact solutions may be obtained as follows

Assume

$$g_{22} = 1 + \theta \quad g_{33} = 1 - \theta \quad g_{23} = 0 \quad \kappa_2 = \kappa_3 = 0 \tag{46}$$

where $|\theta| < 1$ but is not necessarily small Equation (44) becomes

$$2\theta\theta''(1 - \theta^2) + \theta'^2(1 + \theta^2) = 0$$

which integrates to give

$$\xi = x_1 + x_4 = \mathrm{A}\int^{\theta}\left(\frac{t}{1-t^2}\right)^{\frac{1}{2}} dt \tag{47}$$

It follows from this that unless θ is constantly zero it will steadily increase (or decrease) to ± 1 and will attain one of these values for a finite value of ξ Hence there can be no plane gravitational wave of this type for which the determinant g does not vanish for some finite value of ξ

For electromagnetic waves we generalise Eddington's result by assuming

$$g_{22} = g_{33} = -1 + \theta \qquad g_{23} = 0 \tag{48}$$

Equation (44) may then be written

$$\sqrt{(1-\theta)}\frac{d^2}{d\xi^2}\sqrt{(1-\theta)} = -4\pi\gamma(\kappa_2'^2 + \kappa_3'^2) \tag{49}$$

Suppose that when $\xi = 0$ $\theta' = 0$ and $\theta = 0$, then since the right hand side is negative and in general not zero $d/d\xi\sqrt{(1-\theta)}$ is zero for $\xi = 0$ and decreases at a finite rate as ξ increases It follows that θ will attain the value 1 for a finite value of ξ

A slight modification of this argument shows that the conclusion is not substantially affected if the wave is a pulse so that κ_2 and κ_3' vanish except for a small range of values of ξ The root of the difficulty does not lie in the propagation of an infinite *train* of waves, but rather in the propagation of a wave-front of infinite extent

It appears therefore that the relativity theory of light must be approached by way of the study of divergent waves The importance of the problem hardly needs emphasis If light cannot be propagated without change of wave-form we should know the measure of that change in order to ascertain whether it is likely to give rise to observable effects in nature

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Electronic Orbits on the Relativity Theory

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The problem of this paper is to determine the possible circular orbits of a charged electron about a charged nucleus

From the point of view of the older theories the problem is very simple. Let the mass and charge of the nucleus be m and e, and of the electron m' and e', the masses being positive but the charges either positive or negative Write—

$$(1) \qquad \lambda = \frac{e}{m\kappa^{\frac{1}{2}}}, \quad \lambda' = \frac{e'}{m'\kappa^{\frac{1}{2}}},$$

where κ is the constant of gravitation The effect of the charges may be regarded as a modification of the masses, and the two bodies will attract according to the inverse square law as if the product of their masses were $mm'(1 - \lambda\lambda')$ If the charges are of unlike sign, or of like sign and such that $\lambda\lambda' < 1$, this effective mass product will be positive and a circular orbit will be possible for every radius, otherwise no circular orbits are possible.

On the relativity theory the inverse square law is no longer accurately obeyed, particularly for small distances, and the problem is much less simple. In its exact form its solution seems to be impossible in the present state of knowledge, and the present investigation is based on the assumption that the effect of the reaction on the nucleus may be neglected, so that the latter may be regarded as fixed in position This is a serious limitation, but, pending a more exact solution, the results may serve as an indication of the kind of results which may be expected on the relativity theory and of the extent to which these differ from the results of the older theories

The field of the nucleus is defined by*

$$(2) \qquad ds^2 = -\gamma^{-1} dr^2 - r^2 d\theta^2 - r^2 \sin^2\theta \, d\phi^2 + \gamma c^2 dt^2$$

where

$$\gamma = 1 - \frac{2\kappa m}{c^2 r} + \frac{\kappa e^2}{c^4 r}$$

Writing

$$(3) \qquad \frac{\kappa m}{c^2} = a$$

we have

$$(4) \qquad \gamma = 1 - \frac{2a}{r} + \lambda^2 \frac{a^2}{r^2}$$

The equations of motion of an electron in this field have been given† in a form which when simplified for circular orbits in the equatorial plane $\theta = \frac{1}{2}\pi$ become

$$-r\left(\frac{d\phi}{ds}\right)^2 + \frac{1}{2}c^2 \frac{d\gamma}{dr}\left(\frac{dt}{ds}\right)^2 = \frac{e\epsilon}{cm r^2}\frac{dt}{ds}$$

$$r^2\left(\frac{d\phi}{ds}\right)^2 - c^2\gamma\left(\frac{dt}{ds}\right)^2 + 1 = 0$$

Writing

$$(5) \qquad c\frac{dt}{ds} = \frac{1}{Z}$$

and using the notation set out above these become

$$(6) \qquad -r^2 Z\left(\frac{d\phi}{ds}\right)^2 + \frac{a}{r}\left(1 - \lambda^2 \frac{a}{r}\right) = \lambda\lambda \frac{a}{r} Z$$

$$(7) \qquad r^2 Z^2\left(\frac{d\phi}{ds}\right)^2 - \left(1 - \frac{2a}{r} + \lambda^2 \frac{a^2}{r^2}\right) + Z^2 = 0$$

On addition we have

$$(8) \qquad Z^2 - \lambda\lambda \frac{a}{r} Z - \left(1 - \frac{3a}{r} + 2\lambda^2 \frac{a^2}{r^2}\right) = 0$$

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* **Nordstrom**, 'On the Energy of the Gravitational Field on Einstein's Theory' 'Proc Ac. Amsterdam' vol 20 p 1236 (1918)

† **G B. Jeffery** 'The Field of an Electron on Einstein's Theory of Gravitation' 'Roy Soc Proc' A vol 99 pp 123 134 (1921) equations 26 and 31 A factor 4π is omitted as e ε are now measured in electrostatic c g s units

The necessary and sufficient conditions for a real orbit are (i) $d\phi/ds$ must be real and (ii) dt/ds must be real and positive Thus from (7) and (8) we see that r must have a value such that

$$\frac{r^2}{a} - \frac{2r}{a} + \lambda^2 > 0 \tag{9}$$

while (8) has a positive real root for Z less than the positive value of

$$\sqrt{\left((1 - \frac{2a}{r} + \lambda^2 \frac{a^2}{r^2}\right)} \tag{10}$$

If the charges on the electron and nucleus are of opposite sign $\lambda\lambda < 0$ and the conditions that (8) may have a root satisfying the conditions laid down are

$$\frac{r^2}{a^2} - \frac{3r}{a} + 2\lambda^2 > 0 \tag{11}$$

with either

$$(1 - \lambda\lambda)\frac{r}{a} \quad 2\lambda(1 \quad \lambda^2)\frac{r}{a} + \lambda^4(1 - \lambda^2) < 0 \tag{12}$$

or

$$\frac{r}{a} > \lambda^2 \tag{13}$$

Now either (12) by itself or (11) with (13) implies (9) Hence the necessary and sufficient conditions to be satisfied by r in this case are (11) and either (12) or (13) The problem is now reduced to the establishment of inequalities between the roots of quadratics and the work need not be set out in detail The results are shown in Table I in which

$$\frac{a_1}{a} \quad \frac{a_2}{a} = \frac{\lambda^2(1 - \lambda^2) \pm \lambda^2\sqrt{\{\lambda^2(1 - \lambda^2)(\lambda^2 \quad 1)\}}}{1 \quad \lambda^2\lambda^2} \tag{14}$$

$$\frac{b_1}{a} \quad \frac{b_2}{a} = \frac{3 \pm \sqrt{(9 - 8\lambda)}}{2} \tag{15}$$

Of the two expressions on the left hand side in each case the first corresponds to the positive and the second to the negative sign of the radical on the right-hand side

If the charges on the electron and nucleus are of the same sign, $\lambda\lambda > 0$ For certain values of r, (8) will have *two* roots satisfying the conditions laid down This means that for these values of r the orbit can be described with either of two different velocities This circumstance does not appear to have any great physical significance and we will determine the conditions that (8) may have at least one appropriate root These are easily seen to be as follows If

(16) $$\frac{r^2}{a^2} - \frac{3r}{a} \quad \lambda^2 > 0$$

then we must have

(17) $$(1 - \lambda\lambda^2)\frac{r}{a^2} - 2\lambda^2(1 - \lambda^2)\frac{r}{a} + \lambda^4(1 - \lambda^2) > 0$$

and

(18) $$\frac{r}{a} > \lambda^2$$

On the other hand if

(19) $$\frac{r^2}{a} - \frac{3r}{a} + \lambda^2 < 0$$

then we have

(20) $$\frac{r}{a} - \frac{3r}{a} + 2\lambda^2 + \frac{\lambda^2\lambda^2}{4} > 0$$

with either

(21) $$(1 \quad \lambda\lambda\ )\frac{r^2}{a^2} \quad 2\lambda^2(1 \quad \lambda^2)\frac{r}{a} + \lambda^4(1 - \lambda^2) < 0$$

or

(22) $$\frac{r}{a} \quad \lambda^2 + \frac{\lambda\lambda}{2}$$

It may be shown that either set of conditions implies (9) and further by adding $\lambda^2\lambda^2$ times the left hand side of (20) to the left hand side of (21) that (21) implies (20) The conditions may conveniently be put in the three alternative groups —(i) (16) (17) (18) (ii) (19) (21) (iii) (19) (20) (22)

Table I

		$\lambda^2 > 1$		$\lambda < 1$
$\lambda^2 > \frac{1}{4}$		All values of r		$r > a_2$
$\frac{1}{4} > \lambda^2 > 1$	or	$> b_1$ $r < b_2$	r	$r > b$ $b_2 > r > a_2$
$1 > \lambda^2$	or	$r > b$ $< a$		$r > b_1$

Again the problem is reduced to the establishment of inequalities between the roots of quadratics, but the ranges of possible values of r vary for different values of λ and λ' in a more complicated way than when the electron and nucleus have charges of opposite sign The results are shown in Table II in which a_1, a_2, b_1, b_2 have the values defined by (14) and (15), while

$$\frac{c_1}{a}, \ \frac{c_2}{a} = \frac{3 \pm \sqrt{(9 - 8\lambda^2 - \lambda^2\lambda'^2)}}{2} \tag{23}$$

The table is divided into a number of rectangles and rectangular polygons, each corresponding to the range or ranges of r printed within it Values of $\lambda^2\lambda'^2$ are shown along the top of the table and are indicated by the following symbols

$$\mathrm{A}_1, \ \mathrm{A}_2 = \frac{5 - 4\lambda^2 \pm \sqrt{(25 - 24\lambda^2)}}{2},$$

$$\mathrm{B}_1, \ \mathrm{B}_2 = \frac{3 - 2\lambda^2 \pm \sqrt{(9 - 8\lambda^2)}}{2},$$

$$\mathrm{C} = 9 - 8\lambda^2$$

It will be noted that some of these values occur more than once, but in reading the table from left to right for any given range of values of λ^2, any values of $\lambda^2\lambda'^2$ which are not represented by a vertical rule are to be disregarded The remaining values of $\lambda^2\lambda'^2$ are then in decreasing order of magnitude for the range of values of λ^2 in question

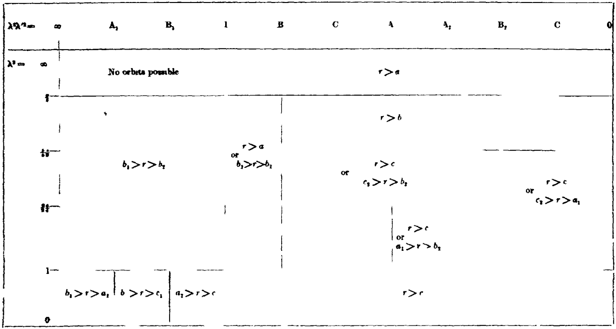
A comparison of these results with those of the older theories may be stated briefly as follows in Table I orbits are possible for all values of r without restriction, in Table II to the right of the vertical double rule orbits are possible for all values of r, but to the left of the double rule no orbits are possible

All these results are subject to the assumption that the nucleus remains fixed in position, that is to say that its mass is large compared with that of the electron But the radii of possible orbits depend only on λ and λ', the ratios of charge to mass Hence the results represent a valid approximation provided m/m' is large

If the electron and nucleus are conceived to be of finite size, there is a further condition to be satisfied—that the radius of the orbit cannot be less than the sum of the radii of the electron and nucleus

If $\lambda^2 > 1$ the field represented by (2) has only a point singularity, but if $\lambda^2 < 1$ the singularity is more complicated There are two spherical surfaces on which ds becomes infinite owing to the vanishing of γ The region between

Table II


$\lambda^2\lambda'^2 =$
∞
A_1
B_1
1
B
C
A
A_2
B_2
C
0
$\lambda^2 =$
∞
[illegible]
[illegible]
[illegible]
1
0
No orbits possible
$r > a$
$r > b$
$b_1 > r > b_2$
$r > a$ or $b_1 > r > b_2$
$r > c$ or $c_1 > r > b_2$
$r > c$ or $c_2 > r > a_1$
$r > c$ or $a_1 > r > b_2$
$b_1 > r > a_2$
$b > r > c_1$
$a_2 > r > c$
$r > c$

these surfaces is excluded by condition (9) It will be noted that in every case this condition is satisfied in virtue of other and wider conditions Hence none of the orbits given lies within this region In only one case do the orbits specified lie in the region within the inner singular surface—a region whose physical existence may well be questioned—viz $\lambda^2 < 1$ $\lambda'^2 > 1$ for electron and nucleus of opposite charges (Table I) $r < a_1$

If $\lambda^2 < 1$ there will be corresponding singular surfaces for the electron but the radii of these will be multiples of the a corresponding to the electron and since its mass is small compared with that of the nucleus it appears from (3) that this will be small compared with a

The results of this paper are somewhat suggestive of Bohr s quantised orbits The resemblance is entirely superficial Indeed for the hydrogen nucleus and the electron of nature λ^2 and λ'^2 are large and by Table I orbits are possible with any radii whatever

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The Motion of Two Spheres in a Viscous Fluid

By Margaret Stimson and G B Jeffery

(Communicated by Prof I N G Filon F R S —Received January 15 1926)

The problem of this paper is to determine the motion set up in a viscous fluid at rest at infinity by two solid spheres (equal or unequal) moving with equal small constant velocities parallel to their line of centres The same analysis is immediately applicable to the corresponding problem in which the spheres are fixed and the fluid streams past them with constant velocity The solution is based on the determination of Stokes stream function for the motion of the fluid and from this the forces necessary to maintain the motion of the spheres are calculated

§ 1 *The Motion of a Symmetrical Solid in a Viscous Fluid*

If ω z are cylindrical co ordinates[*] and u v the corresponding components of velocity of the fluid these are expressed in terms of Stokes stream function by

$$u = \frac{1}{\tilde{\omega}} \frac{\partial \psi}{\partial z} \qquad v = - \frac{1}{\tilde{\omega}} \frac{\partial \psi}{\partial \tilde{\omega}} . \tag{1}$$

---

[*] For $\tilde{\omega}$ throughout this paper read ϖ

Neglecting the inertia terms, the equations of slow steady motion are

$$(2)\qquad \frac{\partial p}{\partial z} = \kappa\nabla^2 w \qquad \frac{\partial p}{\partial \varpi} = \kappa\left(\nabla^2 u - \frac{u}{\varpi^2}\right)$$

where p is the mean pressure, κ the coefficient of viscosity, and

$$(3)\qquad \nabla^2 \equiv \frac{1}{\varpi}\frac{\partial}{\partial \varpi}\left(\varpi\frac{\partial}{\partial \varpi}\right) + \frac{\partial^2}{\partial z^2}$$

If

$$(4)\qquad \Phi^2 \equiv \varpi\frac{\partial}{\partial \varpi}\left(\frac{1}{\varpi}\frac{\partial}{\partial \varpi}\right) + \frac{\partial^2}{\partial z^2}$$

we note that

$$(5)\qquad \nabla^2\left(\frac{1}{\varpi}\frac{\partial \psi}{\partial \varpi}\right) = \frac{1}{\varpi}\frac{\partial}{\partial \varpi}\Phi^2(\psi)$$

and

$$(6)\qquad \nabla^2\left(\frac{1}{\varpi}\frac{\partial \psi}{\partial z}\right) = \frac{1}{\varpi}\frac{\partial}{\partial z}\Phi^2(\psi) + \frac{1}{\varpi^3}\frac{\partial \psi}{\partial z}$$

Eliminating p from (2) we find as the differential equation satisfied by ψ

$$(7)\qquad \Phi^4(\psi) = 0$$

Now the operator Φ^2 is linear in z The ordinary theory of linear partial differential equations with constant coefficients is applicable to an extent sufficient to show that a solution of (7) is

$$\psi = \psi_1 + z\frac{\partial \psi_2}{\partial z},$$

where ψ_1 and ψ_2 are any solutions of $\Phi^2\psi = 0$ Again since Φ^2 is linear in z we may, without loss of generality, replace this by

$$(8)\qquad \psi = \psi_1 + z\psi_2$$

If the solid is moving with velocity V in the positive direction of the z axi the surface conditions to be satisfied by ψ are

$$(9)\qquad \frac{\partial \psi}{\partial z} = 0, \qquad \frac{\partial \psi}{\partial \varpi} = -\varpi \mathrm{V}$$

Denoting the direction of the outward drawn normal to the surface of the solid by n, these may be replaced by

$$(10)\qquad \psi + \tfrac{1}{2}\varpi^2\mathrm{V} = 0, \qquad \frac{\partial}{\partial n}\left(\psi + \tfrac{1}{2}\varpi^2\mathrm{V}\right) = 0$$

The components of fluid stress are given by

$$\widehat{zz} = -p + 2\kappa\frac{\partial v}{\partial z} = -p - \frac{2\kappa}{\varpi}\frac{\partial^2\psi}{\partial z\partial\varpi}$$

$$\widehat{\varpi z} = \kappa\left(\frac{\partial u}{\partial z} + \frac{\partial v}{\partial\varpi}\right) = \kappa\left(\frac{1}{\varpi}\frac{\partial^2\psi}{\partial z^2} - \frac{\partial}{\partial\varpi}\left(\frac{1}{\varpi}\frac{\partial\psi}{\partial\varpi}\right)\right)$$

The component parallel to the z axis of the stress on the surface of the solid is

$$\begin{aligned}\widehat{zn} &= -p\frac{\partial\varpi}{\partial s} - \kappa\left\{\frac{2}{\varpi}\frac{\partial\varpi}{\partial s}\frac{\partial^2\psi}{\partial z\partial\varpi} + \frac{1}{\varpi}\frac{\partial z}{\partial s}\frac{\partial^2\psi}{\partial z^2} - \frac{\partial z}{\partial s}\frac{\partial}{\partial\varpi}\left(\frac{1}{\varpi}\frac{\partial\psi}{\partial\varpi}\right)\right\}\\ &= -p\frac{\partial\varpi}{\partial s} - \kappa\left\{\frac{2}{\varpi}\frac{\partial}{\partial s}\left(\frac{\partial\psi}{\partial z}\right) - \frac{1}{\varpi}\frac{\partial z}{\partial s}\Phi^2(\psi)\right\}\\ &= -p\frac{\partial\varpi}{\partial s} + \frac{\kappa}{\varpi}\frac{\partial z}{\partial s}\Phi^2(\psi)\end{aligned}$$

The total force exerted by the fluid on the solid is

$$Z = -2\pi\int p\varpi\frac{\partial\varpi}{\partial s}ds + 2\pi\kappa\int\frac{\partial z}{\partial s}\Phi^2(\psi)\,ds$$

the integrals being taken round the meridian section of the solid in a direction making a positive right angle with the direction n Integrating the first integral by parts noting that $\varpi = 0$ at the limits and using (2) we obtain

$$Z = \kappa\pi\int\varpi^3\frac{\partial}{\partial n}\left(\frac{\Phi^2(\psi)}{\varpi^2}\right)ds \tag{11}$$

where n is the direction of the normal drawn outwards from the solid and the integral is taken round the meridian section in a sense making a positive right angle with n

§2 *Special Co-ordinates*

For the problem of two spheres we take ξ η as curvilinear co-ordinates in the meridian plane where

$$\xi + i\eta = \log\frac{\varpi + i(z+a)}{\varpi + i(z-a)} \tag{12}$$

so that

$$\varpi = \frac{a\sin\eta}{\cosh\xi - \cos\eta} \qquad z = \frac{a\sinh\xi}{\cosh\xi - \cos\eta} \tag{13}$$

and the surfaces obtained by rotating the curves $\xi = \text{const}$ about the axis of z are a family of spheres having $z = 0$ (or $\xi = 0$) for a common radical plane

Two spheres external to each other will be defined by $\xi = \alpha$, $\xi = \beta$ $(\alpha > 0,\ \beta < 0)$ and α, β and the constant a may be chosen so that these spheres have any radii and any centre distance greater than the sum of their radii In fact if the spheres are of radii r_1, r_2 and have their centres at distances d_1, d_2 from and on opposite sides of the origin then

$$(14)\qquad \begin{aligned} r_1 &= a \operatorname{cosech} \alpha, & r_2 &= -a \operatorname{cosech} \beta \\ d_1 &= a \coth \alpha & d_2 &= -a \coth \beta \end{aligned}$$

Writing $\cos \eta = \mu$ we have in these co ordinates

$$(15)\qquad \Phi^2 \equiv \frac{(\cosh \xi - \mu)}{a^2}\left\{\frac{\partial}{\partial \xi}\left((\cosh \xi - \mu)\frac{\partial}{\partial \xi}\right) + (1-\mu^2)\frac{\partial}{\partial \mu}\left((\cosh \xi - \mu)\frac{\partial}{\partial \mu}\right)\right\}.$$

A solution of $\phi^2(\psi) = 0$ has been given[*] in the form

$$(16)\qquad \psi = (\cosh \xi - \mu)^{-\frac{1}{2}} \Sigma \{a_n \cosh (n + \tfrac{1}{2}) \xi + b_n \sinh (n + \tfrac{1}{2}) \xi\} V_n$$

in which with the usual notation for Legendre functions

$$(17)\qquad V_n = P_{n-1}(\mu) - P_{n+1}(\mu)$$

V_n satisfies the differential equation

$$(18)\qquad (1 - \mu^2)\frac{d^2 V_n}{d\mu^2} + n(n + 1) V_n = 0$$

and the recurrence relation

$$(19)\qquad \mu V_n = \frac{n-1}{2n-1} V_{n-1} + \frac{n+2}{2n+3} V_{n+1}$$

Combining two expressions of the type (16) in accordance with (8) and simplifying the result by means of (19) we obtain a solution of (7) in the form

$$(20)\qquad \psi = (\cosh \xi - \mu)^{-\frac{3}{2}} \Sigma U_n V_n$$

where V_n is defined by (17) and

$$(21)\qquad \begin{aligned} U_n = {} & A_n \cosh (n - \tfrac{1}{2}) \xi + B_n \sinh (n - \tfrac{1}{2}) \xi \\ & + C_n \cosh (n + \tfrac{3}{2}) \xi + D_n \sinh (n + \tfrac{3}{2}) \xi \end{aligned}$$

Accordingly (20) is the appropriate form in these co ordinates for the stream function for the motion of a viscous fluid

§ 3 *Determination of the Stream Function*

Writing $\chi = \Sigma U_n V_n$ the surface conditions (10) become

$$(22)\qquad \chi = -\tfrac{1}{2}\frac{a^2 V (1 - \mu^2)}{(\cosh \xi - \mu)^{\frac{3}{2}}}, \qquad \frac{\partial \chi}{\partial \xi} = \tfrac{3}{4}\frac{a^2 V (1 - \mu^2) \sinh \xi}{(\cosh \xi - \mu)^{\frac{5}{2}}}$$

---

[*] G B Jeffery Roy Soc Proc A vol 87 p 115 (1912)

By means of the relation

$$(1-\mu^2)\,\mathrm{P}_n(\mu)=\frac{(n+1)(n+2)}{(2n+1)(2n+3)}\,\mathrm{V}_{n+1}-\frac{n(n-1)}{(2n+1)(2n-1)}\,\mathrm{V}_n\,,$$

the right hand sides of these expressions may be expanded in series of V_n we obtain

$$\chi=-\frac{a^2\mathrm{V}}{\sqrt{2}}\sum_{n=1}^{\infty}\frac{n(n+1)}{2n+1}\left\{\frac{e^{\mp(n-\frac{1}{2})\xi}}{2n-1}-\frac{e^{\mp(n+\frac{3}{2})\xi}}{2n+3}\right\}\mathrm{V}_n, \tag{23}$$

$$\frac{\partial\chi}{\partial\xi}=\pm\frac{a^2\mathrm{V}}{2\sqrt{2}}\sum_{1}^{\infty}\frac{n(n+1)}{2n+1}\{e^{\mp(n-\frac{1}{2})\xi}-e^{\mp(n+\frac{3}{2})\xi}\}\,\mathrm{V}_n \tag{24}$$

where the upper of the alternative signs is to be taken throughout if $\xi>0$ and the lower if $\xi<0$ Writing

$$\frac{a^2\mathrm{V}n(n+1)}{\sqrt{2}\,(2n-1)(2n+1)(2n+3)}=k \tag{25}$$

we have the following equations to determine the coefficients in (21) for $n>1$

$$\left\{\begin{aligned}
&\mathrm{A}_n\cosh(n-\tfrac{1}{2})\alpha+\mathrm{B}_n\sinh(n-\tfrac{1}{2})\alpha\\
&\qquad+\mathrm{C}_n\cosh(n+\tfrac{3}{2})\alpha+\mathrm{D}_n\sinh(n+\tfrac{3}{2})\alpha\\
&\qquad\qquad=-k\{(2n+3)\,e^{-(n-\frac{1}{2})\alpha}-(2n-1)\,e^{-(n+\frac{3}{2})\alpha}\}\\
&\mathrm{A}_n\cosh(n-\tfrac{1}{2})\beta+\mathrm{B}_n\sinh(n-\tfrac{1}{2})\beta\\
&\qquad+\mathrm{C}_n\cosh(n+\tfrac{3}{2})\beta+\mathrm{D}_n\sinh(n+\tfrac{3}{2})\beta\\
&\qquad\qquad=-k\{(2n+3)\,e^{(n-\frac{1}{2})\beta}-(2n-1)\,e^{(n+\frac{3}{2})\beta}\}\\
&(2n-1)\{\mathrm{A}_n\sinh(n-\tfrac{1}{2})\alpha+\mathrm{B}_n\cosh(n-\tfrac{1}{2})\alpha\}\\
&\qquad+(2n+3)\{\mathrm{C}_n\sinh(n+\tfrac{3}{2})\alpha+\mathrm{D}_n\cosh(n+\tfrac{3}{2})\alpha\}\\
&\qquad\qquad=(2n-1)(2n+3)\,k\{e^{-(n-\frac{1}{2})\alpha}-e^{-(n+\frac{3}{2})\alpha}\}\\
&(2n-1)\{\mathrm{A}_n\sinh(n-\tfrac{1}{2})\beta+\mathrm{B}_n\cosh(n-\tfrac{1}{2})\beta\}\\
&\qquad+(2n+3)\{\mathrm{C}_n\sinh(n+\tfrac{3}{2})\beta+\mathrm{D}_n\cosh(n+\tfrac{3}{2})\beta\}\\
&\qquad\qquad=-(2n-1)(2n+3)\,k\{e^{(n-\frac{1}{2})\beta}-e^{(n+\frac{3}{2})\beta}\}
\end{aligned}\right. \tag{26}$$

Solving these equations for A_n, B_n C_n, D_n and writing

$$\Delta=4\sinh^2(n+\tfrac{1}{2})(\alpha-\beta)-(2n+1)^2\sinh^2(\alpha-\beta) \tag{27}$$

we have

$$\begin{aligned}
\Delta\,\mathrm{A}_n=(2n+3)\,k\,\{&4e^{-(n+\frac{1}{2})(\alpha-\beta)}\sinh(n+\tfrac{1}{2})(\alpha-\beta)\\
&+(2n+1)^2e^{(\alpha-\beta)}\sinh(\alpha-\beta)\\
&+2(2n-1)\sinh(n+\tfrac{1}{2})(\alpha-\beta)\cosh(n+\tfrac{1}{2})(\alpha+\beta)\\
&-2(2n+1)\sinh(n+\tfrac{3}{2})(\alpha-\beta)\cosh(n-\tfrac{1}{2})(\alpha+\beta)\\
&-(2n+1)(2n-1)\sinh(\alpha-\beta)\cosh(\alpha+\beta)\},
\end{aligned} \tag{28}$$

$$
\begin{aligned}
(29)\quad \Delta\,\mathrm{B}_n = -(2n+3)k\{&2(2n-1)\sinh(n+\tfrac{1}{2})(\alpha-\beta)\sinh(n+\tfrac{1}{2})(\alpha+\beta)\\
&-2(2n+1)\sinh(n+\tfrac{3}{2})(\alpha-\beta)\sinh(n-\tfrac{1}{2})(\alpha+\beta)\\
&+(2n+1)(2n-1)\sinh(\alpha-\beta)\sinh(\alpha+\beta)\}
\end{aligned}
$$

$$
\begin{aligned}
(30)\quad \Delta\,\mathrm{C}_n = -(2n-1)k\{&4e^{(n+\frac{1}{2})(\alpha-\beta)}\sinh(n+\tfrac{1}{2})(\alpha-\beta)\\
&-(2n+1)^2e^{(\alpha-\beta)}\sinh(\alpha-\beta)\\
&+2(2n+1)\sinh(n-\tfrac{1}{2})(\alpha-\beta)\cosh(n+\tfrac{3}{2})(\alpha+\beta)\\
&-2(2n+3)\sinh(n+\tfrac{1}{2})(\alpha-\beta)\cosh(n+\tfrac{1}{2})(\alpha+\beta)\\
&+(2n+1)(2n+3)\sinh(\alpha-\beta)\cosh(\alpha+\beta)\}
\end{aligned}
$$

$$
\begin{aligned}
(31)\quad \Delta\,\mathrm{D}_n = (2n-1)k\{&2(2n+1)\sinh(n-\tfrac{1}{2})(\alpha-\beta)\sinh(n+\tfrac{3}{2})(\alpha+\beta)\\
&-2(2n+3)\sinh(n+\tfrac{1}{2})(\alpha-\beta)\sinh(n+\tfrac{1}{2})(\alpha+\beta)\\
&+(2n+1)(2n+3)\sinh(\alpha-\beta)\sinh(\alpha+\beta)\}
\end{aligned}
$$

Thus the stream function is completely determined

In the special case of equal spheres $\beta = -\alpha$ the coefficients B_n and D vanish, and

$$(32)\qquad \mathrm{A}_n = -(2n+3)k\,\frac{2(1-e^{-(2n+1)\alpha})+(2n+1)(e^{2\alpha}-1)}{2\sinh(2n+1)\alpha+(2n+1)\sinh 2\alpha}$$

$$(33)\qquad \mathrm{C}_n = (2n-1)k\,\frac{2(1-e^{-(2n+1)\alpha})+(2n+1)(1-e^{-2\alpha})}{2\sinh(2n+1)\alpha+(2n+1)\sinh 2\alpha}$$

§ 4 *The Forces on the Spheres*

In order to calculate the forces necessary to maintain the motion of the spheres, we consider the contribution to the integral (11) arising from the nth term of (20) Substituting in (15) we have

$$
\begin{aligned}
\frac{1}{\omega^2}\Phi^2(\psi) = \frac{(\cosh\xi-\mu)^{\frac{5}{2}}}{a^4(1-\mu^2)}\Bigg[&\mathrm{V}_n\left\{\frac{d^2\mathrm{U}_n}{d\xi^2}-\frac{2\sinh\xi}{\cosh\xi-\mu}\frac{d\mathrm{U}_n}{d\xi}+\frac{3(\cosh\xi+3\mu)}{4(\cosh\xi-\mu)}\mathrm{U}_n\right\}\\
&-(1-\mu^2)\,\mathrm{U}_n\left\{\frac{d^2\mathrm{V}_n}{d\mu^2}+\frac{2}{\cosh\xi-\mu}\frac{d\mathrm{V}_n}{d\mu}\right\}\Bigg]
\end{aligned}
$$

Differentiating with respect to ξ and inserting in the integral (11) we remove the terms containing the second differential coefficient of V_n by means of (18) and those containing the first differential coefficient by an integration by parts, noting that V_n vanishes for $\mu = \pm 1$ The integration with respect to μ now depends on

$$\int_{-1}^{+1}\frac{\mathrm{V}_n\,d\mu}{(\cosh\xi-\mu)^{\frac{1}{2}}} = 2\sqrt{2}\left\{\frac{e^{\mp(n-\frac{1}{2})\xi}}{2n-1}-\frac{e^{\mp(n+\frac{3}{2})\xi}}{2n+3}\right\}$$

where the upper or lower signs are taken as $\xi \gtrless 0$, and on integrals derived from the above by differentiation with respect to ξ. Finally, on inserting the expression in (21) for U_n, and summing for n, we have for the force necessary to maintain the motion of the sphere $\xi = \alpha$

$$F_1 = -\frac{\kappa\pi 2\sqrt{2}}{a}\sum_{n=1}^{\infty}(2n+1)(A_n + B_n + C_n + D_n) \tag{34}$$

and for the sphere $\xi = \beta$

$$F_2 = -\frac{\kappa\pi 2\sqrt{2}}{a}\sum_{n=1}^{\infty}(2n+1)(A_n - B_n + C_n - D_n) \tag{35}$$

where A_n, B_n, C_n, D_n have the values given in (28)–(31).

For equal spheres these forces are equal, and we may conveniently write each of them in the form

$$F = 6\pi\kappa r V\lambda, \tag{36}$$

where r is the radius of either sphere and is given by (14), and λ is a coefficient which on using (32) and (33) may be written in the form

$$\lambda = \tfrac{4}{3}\sinh\alpha\sum_{n=1}^{\infty}\frac{n(n+1)}{(2n-1)(2n+3)}\left\{1 - \frac{4\sinh^2(n+\frac{1}{2})\alpha - (2n+1)^2\sinh^2\alpha}{2\sinh(2n+1)\alpha + (2n+1)\sinh 2\alpha}\right\} \tag{37}$$

By Stokes's well known result, the force necessary to maintain the motion of a single sphere of radius r with velocity V is $6\pi\kappa r V$. Thus λ is the ratio of the force necessary to maintain the motion of either sphere in the presence of the other to the force which would be necessary to maintain its motion with the same velocity if the other sphere were at an infinite distance.

From (14) we see that the ratio of the centre distance to the diameter of either sphere is equal to $\cosh\alpha$. The values of λ corresponding to different values of this ratio are shown in the table

α	$\frac{\text{Centre Distance}}{\text{Diameter}}$	λ
0·5	1·128	0·663
1·0	1·543	0·702
1·5	2·352	0·768
2·0	3·762	0·836
2·5	6·132	0·892
3·0	10·068	0·931
∞	∞	1·000

The L Emission Series of Mercury

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(Communicated by J H Jeans Sec R S —Received November 30 1925)

Introduction

The L emission series of most of the heavy elements from ytterbium to uranium have been investigated by Coster[*] and by Dauvillier[†] but their tables of results do not include measurements for some of the radio active elements and for mercury Muller[‡] in 1921 by means of a tube of the gas filled type and a liquid mercury target overcame the inherent difficulty regarding mercury viz that of the rapid volatilization of the mercury from the face of the anticathode

It has been found possible to prepare targets amalgamated with mercury which are sufficiently lasting to enable their use in a tube of the hot filament type, by this means measurements of the wave lengths of the emission lines have been made with an accuracy exceeding that of Muller In addition several new lines have been measured and an attempt made to clear up a certain amount of confusion which exists regarding the designation of some of the lines of the L spectra of elements of higher atomic number

Apparatus

The apparatus was essentially similar to that used previously by one of us,[§] and will be described here very briefly The tube was of the metal type and

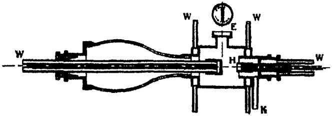

Fig 1

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[*] Z. f Physik vol 6 p 185 (1921)

[†] Journal de Physique vol 3 p 221 (1922)

[‡] Phil. Mag vol 42 p. 419 (1921)

[§] Eddy Proc. Roy Soc Victoria vol 38 p 1 (1925) designed by Prof Laby for spectroscopic work The main body of the tube (see fig 1) was constructed from brass tubing the filament holder being screwed in to permit of its being readily removed for the replacement of filaments The anode was very light consisting of a hollow cylindrical copper target supported by copper tubes through which a stream of water was passed for cooling purposes The target could be removed readily and a fresh one substituted The cathode and anode portions were connected by a lamp glass these and other joints being made gas tight with Picein and protected from the heat generated in the tube by a system of water jackets W through which water was circulated continuously The target face was inclined at an angle of 86° to the axis of the tube and the rays after leaving the target at almost grazing incidence passed out through a mica window 0 04 mm thick contained in the side tube E which carried a screw thread for attachment to the spectrometer chamber

The filament consisting of a spiral of tungsten wire placed at right angles to the axis of the tube was attached to heavy leads passing through a lamp seal waxed into the cathode The filament hood H served to focus the cathode ray beam on the target and was adjusted until the focal spot as depicted by a pinhole camera photograph taken in line with the slits of the spectrometer showed as a line about 3 mm long and less than 0 5 mm wide In this way a very intense beam was transmitted through the slit system The tube was evacuated through the outlet K by a Cenco oil pump a Gaede rotary mercury pump and a Langmuir condensation pump in series The pumps were kept in operation continuously during the running of the tube The liberation of the occluded gases was greatly diminished by silver plating the metal portions of the tube

The spectrometer was in essentials similar to that described by Rogers[*] and by Martin[†] with some slight modifications for this work The crystal table adapted from a theodolite was screwed to an iron base plate The slit system and the film holder were carried on iron pillars also screwed to this base and the whole was surrounded by a metal cylinder fitting closely on the base plate and closed at the top with a sheet of plate glass The tube was attached to the side of the cylinder so that the window was brought to within 1 cm of the slits The crystal of calcite was rotated by a shaft passing through a stuffing box in the side of the cylinder and turned by a small motor and reduction gear

The tube was excited by a Snook Victor high tension transformer and rectifier, a potential of 30 kilovolts with a current of from 6 to 8 milliamperes being employed; greater currents caused too great a local heating of the focal spot and hence a more rapid disappearance of the mercury.

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[*] Proc Roy Soc Vic vol 34, p 200 (1922)

[†] *Ibid* vol 35 p 164 (1923)

Experiment

Some difficulty was at first met with in preparing a mercury surface which would last for more than an hour's running of the tube, but subsequently a satisfactory coating was produced by wetting the copper surface with mercury nitrate solution, and then leaving the prepared surface standing in liquid mercury for several hours. On removing the surplus mercury and leaving the target for several days, a hard dry amalgam resulted which persisted for upwards of fifteen hours' running of the tube, and permitted several photographs of the whole spectrum being obtained with the one coating.

The films were wrapped in sheets of tissue paper and aluminium leaf, with a total thickness of 0·15 mm; this prevented any action of ordinary light on the film, and absorbed much less radiation than the usual black paper wrapper. "Superspeed" Kodak Duplitized X-ray film was used, with a rear intensifying screen.

The slit width varied between 0·075 and 0·1 mm, and with the former the copper $K\alpha$ doublet ($\delta\lambda = 3{\cdot}9$ X.U.) showed lines on the film distant apart about 0·16 mm.

The wave-lengths of the mercury lines were determined relative to standard lines photographed on the same film. The four strong lines (α, β_1, β_2, γ_1) of the L series of both tungsten and lead were used as reference lines. The lead lines were obtained by substituting a lead-coated target for the mercury target. The tungsten lines were obtained from the tungsten deposit which rapidly formed on either target due to the volatilization of the tungsten filament. Exposures of about 15 minutes were required for a set of reference lines, and about 3½ hours for the whole of the mercury spectrum.

The distances between the lines on the film were measured by a projection method suggested by Prof. Laby and used with success in this laboratory. The film was projected by a lantern on to a vertical screen carried on the platform of a dividing engine. A fine vertical line was ruled on this screen, and by rotating the screw head of the engine this line could be brought into coincidence with the projected lines. The displacements of the platform were read to 0·005 mm. Measurements of each film were made at two magnifications, magnifying powers of from 6 to 10 being used. The film so measured was calibrated in seconds per millimetre of projection by dividing the angular differences between two standard lines by their distance apart, and the means of values obtained form different pairs of lines taken The reflection angle of any unknown line could then be determined from its distance from any (preferably neighbouring) standard line The reflection angles of the standard lines were calculated from their wave lengths taking *d* for calcite as 3029 04 X U The standard values assumed for the tungsten lines were the means of the values obtained by Siegbahn and Dolejsek[*] and by Duane and Patterson[†] and for lead those of Coster[‡]

The projection method of film measurement appears to possess advantages over a comparator method from the point of view of convenience as well as accuracy as the ability to use both eyes in normal light intensities obviates the strain caused by continuo is working with a microscope

Results and Discussion

The results obtained are shown in Table I The probable errors are shown for the five strongest lines the values being the means from at least eight films For the other lines the mean of the results from at least three films is given the accuracy of the values of the fainter lines is considerably less than for the strong lines because of the greater difficulty in making an accurate setting at their centres but the error should in no case exceed 0 5 X U In the third column are entered for comparison the wave lengths obtained by Muller The $\sqrt{\nu/R}$ values as given by our results by Muller and by interpolation from the results of Coster are given in the fourth fifth and sixth columns respectively

It will be seen that our values for the stronger lines agree well with those of Muller especially when the magnitude of his probable errors is considered an exception is β_2 our value being somewhat higher than the interpolated value while that of Muller is lower

Before discussing the disagreement for the fainter lines it will be as well to draw attention to a certain amount of confusion which has existed regarding the relative positions of certain lines in the spectra of the heavy elements Besides the regular shift of the characteristic spectrum towards the shorter wave-lengths with increase in the atomic number of the emitting element there also occur in certain places in the periodic table of the elements changes in the relative intensities and relative positions of particular lines it is thus a difficult matter to name correctly lines which lie close together without the aid of the Moseley diagrams (the graphs of $\sqrt{\nu/R}$ against N) An interesting feature of

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[*] Z f Physik vol 10 p. 159 (1922)

[†] Physical Review, vol 16, p 525 (1920)

[‡] *Loc. cit*

Table I —The L Emission Series of Mercury

Line.	Wave lengths F and T	Wave lengths Muller	Values of $\sqrt{\nu/R}$ F and T	Values of $\sqrt{\nu/R}$ Muller	Values of $\sqrt{\nu/R}$ Interpolated
l	1418 41 X U	1418 3 X U	25 347	25 348	25 340
	1380 6		25 690		
α_2	1249 51 ± 06	1249 7	27 005	27 004	27 001
α_1	1238 48 ± 06	1238 5 ± 3	27 125	27 125	27 126
η	1161 6	1161 9	28 008	28 005	28 016
β_6	1076 8	1077 4	29 091	29 083	29 072
β_4	1069 2	1068 6	29 194	29 202	29 178
β_1	1045 49 ± 06	1045 8 ± 6	29 522	29 519	29 538
β_3	1036 55 ± 08	1037 5 ± 4	29 650	29 637	29 641
β_2	1030 46	1030 1	29 738	29 74	29 725
β_{15}	1030 46		29 738		29 738
β_7	1015 5	1007 8	29 956	30 071	29 950
β_5	1006 7	1007 8	30 067	30 071	30 080
β_{10}	993 6		30 284		30 27
β_9	984 2		30 430		30 42
γ_5	922 9	914 4	31 422	32 56	31 41
	907 6		31 686		
γ_1	893 53 ± 05	893 5 ± 7	31 935	31 935	31 932
	882 9		32 123		
γ_6	872 4		32 320		32 35
γ_2	872 4	869 5	32 320	32 37	32 324
γ_3	866 2	860 5	32 435	32 37	32 435
	856 4		32 621		
γ_4	836 1	834 8	33 014	33 03	32 90

these diagrams is that the graphs of all lines are not parallel and several intersections occur in the region of higher atomic numbers Different workers do not always agree on the point where these intersections take place For the lines β_2 and β_3 it has been shown by Dauvillier, by Coster, and by Rogers,* that coincidence occurs for Pt (N = 78), for higher atomic numbers β_2 being of longer wave length than β_3 The lines β_1, β_2 have been shown coincident by Dauvillier and by Coster for Pb (82) and we were unable to resolve them for this element Rogers found β_4 and β_6 coincident for Pt (78), Coster separated them for Ir (77) and Au (79) but Dauvillier believed them to be coincident for both iridium and platinum In the case of γ_2 and γ_3 Coster, in his first paper,† thought them to cross between Au (79) and Ur (92), in his later paper he places γ_3 on the long wave length side of γ_2 right up to uranium Muller found γ_2 and γ_3 coincident for Hg (80), but it appears he did not resolve these two lines, as his value lies midway between our values, which lie very close to the values interpolated from Coster's later paper (see fig 2) In the case of

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* 'Proc Camb Phys Soc.,' vol 21, p. 430 (1923)

† 'Z f Physik' vol 4, p 178 (1921).

β_7 and β_5, which do not cross according to both Coster and Dauvillier, Muller found a coincidence, actually the graphs for these two lines are diverging in this region, and it appears likely he did not obtain the line measured by us as β_7, which agrees well with the interpolated value.

In the table, β_2 and β_6 are shown as coincident, the former is quite a strong line, the latter a weak one, and it may have been masked by the lateral spreading of β_2 As is evident from fig 2, these two lines should cross in the vicinity of Hg (80) The lines γ_2 and γ_6 are also shown as coincident; on the film γ_2 appeared broader than it should have done if but a single line, but the resolution was not sufficient to prove the existence of two lines Coster found these two lines coincident for Ir (77), Pt (78), and Au (79), and separated them for Tl (81)

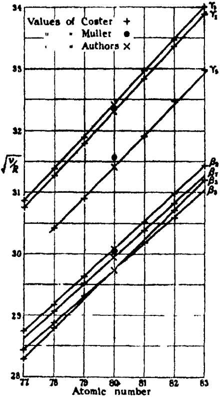

FIG. 2.

The lines shown as β_{10}, β_9 and γ_5 fall very close to the interpolated values, β_{10} has not previously been measured for elements above gold It is difficult to account for the line called by Muller γ_5, as a very faint line of wave length 914 4 X U would not be easily distinguishable in the pronounced blackening of the film due to the selective absorption by the bromine in the photographic emulsion

The bromine K absorption edge was measured at 917 7 X U, which is in fair agreement with the value of Rogers (*loc cit*) 917 8 X U, and of Duane and Blake* 917 9 X U

Many lines found on the films which could be attributed to either first or second order spectra of the K or L series of impurities in the target materials, or portions of the tube or the slit system have not been included in the table

The lines of wave lengths 1380 6, 907 6 882 9 and 856 4 X U have been tentatively allotted to the mercury spectrum It is well known that the energy value of a line (in ν/R units) can be expressed as the difference between the energies of the initial and final levels in the electron transition, consequent upon which the line is produced It is thus possible to allot a line to a transition between two levels Bohr however in the Principle of Selection, has limited the number of possible transitions between different electronic orbits Every orbit has been characterised by three quantum numbers n (k_1, k_2) and transitions are only possible between orbits whose values of k_1 differ by unity, and whose k_2 values differ by zero or unity

The second column of Table II shows the ν/R values of the four lines, the third the differences for the levels which may be concerned in the transition In the fourth column are given the values of n (k_1, k_2) for the orbits mentioned and the changes in the quantum number occasioned by the suggested transition

Table II

Line	ν/R Units	Difference ν/R Units	Change in Quantum Numbers		
1380 6 X U	660 0	661 7 $L_{III}M_{II}$	2(2 2) 3(2 1)	$\delta k_1 = 0$	$\delta k_2 = 1$
907 6	1004 0	1003 7 L_{II} N_{III}	2(2 1) 4(2 2)	0	1
882 9	1032 1	1030 9 L_I N_I	2(1 1) 4(1 1)	0	0
856 4	1064 1	1064 0 L_I N_{IV}	2(1 1) 4(3 2)	2	1

It thus appears that if these four lines do belong to mercury, they are exceptions to the selection principle Apparent exceptions to the principle have been found by Hjalmar for the K rays of the lighter elements and by Auger and Dauvillier* for the L rays of some of the heavier elements and may arise from electron transitions in atoms which have lost more than one electron The line 1380 6 X U lies a little way from the graph of the line called t ' by these last named workers

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* 'Physical Review' vol. 10, p. 697 (1917)

This work was carried out while one of us was a Fred Knight and University Research Scholar In conclusion we wish to express our gratitude to Prof T H Laby and to Mr J S Rogers for their helpful interest and advice during the progress of the investigation and to the latter for his assistance in writing this report

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The Ratios of the Specific Heats of Nitrogen at Atmospheric Pressure and at Temperatures between 10° C *and* −183° C

By J H Brinkworth A R C S M Sc D I C

(Communicated by Prof H L Callendar F R S —Received December 17 1925)

These measurements of the ratios of the specific heats of nitrogen at room and at lower temperatures have been made and the results have been calculated in exactly the same way as those obtained when air and hydrogen were used The latter were described in a former paper (1) in which will be found a description of the apparatus and an account of the method of dealing with the experimental results In the work which follows the same apparatus was employed the only changes being that a new platinum wire (from the same reel) was used on the thermometer and owing to breakage a rather finer quartz suspension had been put on the galvanometer However as the apparatus had to be dismantled for transference to another laboratory I thought it desirable to confirm some of the effects and relationships previously noted therefore a full set of experiments with the four expansion vessels was made at room temperature It may be recalled that the method has been especially worked out using small expansion vessels in order that values of the ratios of the specific heats can be readily obtained at different temperatures Up to the present time work has been restricted to determinations at temperatures below that of the laboratory Several vessels are used in order to allow a correction to be made for a systematic change in the apparent value of the ratio, which depends on the size of the vessel employed

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* 'Comptes Rendus' vol. 176 p 1297 (1923)

The nitrogen was supplied by the British Oxygen Company, and was stated to contain less than ½ of 1 per cent of impurity, mostly oxygen I am indebted to Mr D Newitt for six analyses of gas taken from the apparatus at various times during the course of the experiments All of these show that the percentage impurity was less than the amount stated above

The observations at − 78° C, reduced in the way previously described, are given on p 126 They show the steadiness of the experimental conditions and the accuracy with which these could be reproduced The quantity γ_a, tabulated in the last column, is the apparent value of the ratio of the specific heats calculated from the well-known relation

$$s_p/s_v = \frac{\log p_1/p_2}{\log p_1/p_2 - \log \theta_1/\theta_2}, \tag{A}$$

where p_1 and p_2 are the initial and final pressures in centimetres of mercury, and θ_1 and θ_2 the initial and final temperatures on the absolute scale The values of γ_a thus obtained vary systematically with the size of the vessel used By extrapolating linearly a procedure which has been shown to be extraordinarily accurate over a considerable range in the size of the vessels employed, and which is again confirmed, a value indicated by γ' is deduced This is the apparent value of the ratio which would have been obtained if the measurements had been made using a vessel of infinite volume This extrapolated value still requires two corrections, (*a*) the so-called radiation correction, and (*b*) a theoretical correction

Fundamental Interval, Freezing Point, and Heating Effect Observations in Centimetres of Bridge Wire

Date, 1925	Temp °C	1 cell	2 cells	
14 10	0	705 72	706 11	F P 705 59
	99 985	973 43	973 72	F I 267 78
9 11	0	705 78	706 17	F P 705 65
	99 551	972 33	972 61	F I 267 79

Heating Effects (subtractive)

Date, 1925.	Temp °C	1 cell	2 cells
14 10	0	0·13	0 52
	100	0·10	0 39
20 10	11	0·13	0 51
29·10	− 78	0 16	0 63
4 11	−183	0 17	0 68
9·11	0	0·13	0 52
	100	0 09	0 37

In the two experiments made in 1924, with the apparatus as used in the air and hydrogen experiments the constants of the thermometer were F P = 813 88 and F I = 310 95 The heating effects being 0 58 at 11° C and 0 21 at − 183° C

Reduced Observations

Columns (*a*) and (*d*) give the values of θ_1 and θ_2 expressed in centimetres of bridge wire after the application of all corrections

Column (*b*) gives the bridge wire setting for the observation of θ_2 and (*c*) the resulting kick deflection

October 29 1925 300 c c bulb

p_2	p_1	*a*	*b*	*c*	*d*	θ_2	θ_1	γ_0
75 65	80 590	489 7_	20 4	35	480 08	191 321	194 763	1 3928
	56_	72	2	1	09	325	763	3942
	538	7_	4	29	12	335	763	3927
	518	73	3	2	18	356	766	3951
	496	75	4	8	24	377	773	3953
	465	76	4	0	29	395	777	3964
	442	76	5	8	34	413	777	3961
	416	76	5	1	40	435	777	3953
	392	75	7	26	44	449	773	3950
	369	75	6	_	48	464	773	3951
	344	75	7	2	58	499	773	3952
	322	77	9	29	62	513	780	3933
	290	79	9	13	71	545	788	3921
	273	82	9	8	74	555	799	3949

October 29 1925 35 c c bulb

p_2	p_1	*a*	*b*	*c*	*d*	θ_2	θ_1	γ_0
75 59	80 528	489 78	20 6	17	480 29	191 396	194 786	1 3840
	516	78	8	38	24	378	786	3880
	508	78	6	11	36	421	786	3821
	494	78	5	2	37	425	786	3830
	487	78	6	10	37	425	786	3837
	477	79	5	1½	37	425	789	3852
	466	79	6	9	38	428	789	3859
	454	79	5	−4	44	449	789	3838
	440	79	6	1	48	463	789	3830
	430	79	8	20	46	456	789	3851
	418	79	6	1	48	463	789	3863
	410	78	7	6½	51	474	786	3840
	397	78	7	4	54	485	786	3836

Other values of γ_0 obtained under similar conditions 1 3850, 1 3834, 1 3822, 1 3834 1 3836, 1 3837, 1 3842, 1 3848

Summarised Results for Nitrogen

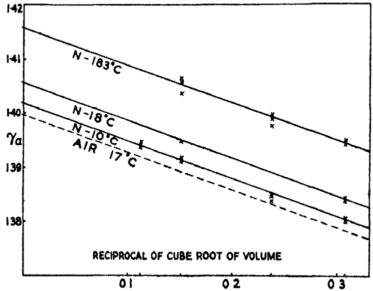
Date, 1925	Vol , c.c	Time secs	No of Obs	p_2, cms	p_1 cms	θ_2, Abs	θ_1 Abs	γ_a Means
15 10	700	0 51	9	76 17	80 975	277 618	282 467	1 3936
16 10	700	0 60	10	76 15	80 916	277 378	282 186	1 3945
16 10	700	1	9	76 17	80 945	277 448	282 242	1 3931
19 10	700	—	8	75 95	80 750	280 000	284 878	1 3935
19 10	700	1	9	75 94	80 743	279 923	284 822	1 3933
20 10	700	—	10	75 19	80 055	278 881	283 862	1 3942
9 11	700	<0 5	7	75 73	80 592	277 538	282 467	1 3945
22 10	300	0 33	10	73 84	78 715	284 132	289 288	1 3918
25 10	300	0 45	9	75 05	79 950	279 285	284 298	1 3911
14 10	75	0 31	10	75 98	80 864	279 273	284 150	1 3851
15 10	75	0 21	10	76 18	81 123	277 229	282 119	1 3840
18 11 24	75	—	10	77 35	82 283	279 450	284 291	1 3849
23 9	35	—	6	74 69	79 560	280 878	285 815	1 3807
29 9	35	0 20	8	76 79	81 765	280 288	285 184	1 3802
29 10	300	—	14	75 65	80 416	191 435	194 777	1 3948
29 10	35	—	8	75 60	80 450	191 408	194 736	1 3838
29 10	35	—	13	75 59	80 454	191 449	194 789	1 3844
4 11	300	1	12	75 65	80 469	88 528	90 117	1 4037
4.11	300	1½-2	8	75 68	80 425	88 524	90 081	1 4020
12 11	300	0 65	9	76 94	81 688	88 785	90 330	1 4058
12.11	300	0 57	9	76 90	81 795	88 758	90 354	1 4065
5 11	75	—	13	75 39	80 257	88 548	90 143	1 3989
11 11	75	—	9	76 44	80 375	88 497	90 084	1 3997
20.11 24	75	—	10	77 36	82 079	88 767	90 283	1 3978
4 11	35	0 37	11	75 70	80 641	88 416	90 012	1 3943
11 11	35	—	12	76 62	81 445	88 637	90 183	1 3951

p_1, p_2, θ_1 and θ_2 are actual observations selected from about the middle of the group giving rise to the mean value of γ_a in the same horizontal row

In the experiments of October 20 with the 700 c c bulb, and those made on October 15, with the 75 c c bulb two cells were used in the battery circuit The actual heating effect at 10° C was thus increased from 0 13 to 0 51 cm and the difference between the heating effects at 0° C and at 100° C increased from 0 03 to 0 13 cm of bridge wire But the correction only depends on the difference between the heating effects at θ_1 and θ_2 and was therefore less than 0 01 cm of bridge wire That is, the additive correction to γ_a was less than one part in 3000, and in all the other experiments on nitrogen it was negligible As the heating effects were constantly re-determined under the actual experimental conditions, and very consistent values were obtained, the correction could always be made with great accuracy, even when it was considerably larger, as it was in my experiments on hydrogen at room temperature.

Actual time measurements were not made in every case as the chronograph was required for other work The large values of the time given in four instances were estimated by direct observation The consistency of the values of γ_a obtained with the largest bulb when the times were varied from less than 0 5 to about 1 second, shows that overshooting does not affect the results Similar evidence was given in my paper on air and hydrogen Probably rather too much cooling has taken place during the interval between the commencement of the expansion and the time at which the galvanometer circuit is made, when this interval is about 1 second in the cases of (*a*) the 700 c c bulb at room temperature and (*b*) the 300 c c bulb at — 183° C

In the figure the mean results obtained with each bulb are plotted against



the reciprocal of a linear dimension of the vessel employed, *i e* the cube root of the volume For the bulbs employed the values of these abscissæ are 0 1128, 0 1516, 0 2371 and 0 3072 respectively The linear relation previously shown to exist is amply verified The points given by the intersections of these lines with that of infinite volume give values of γ at the three temperatures at which experiments were made

These values are, in the case of nitrogen, 1 4019 at 10° C , 1 4056 at — 78° C , and 1 4158 at − 183° C The dotted line shows results previously obtained with air and is included for comparison

The values of γ require two further corrections (*a*) the so-called radiation correction (*b*) the theoretical correction

(*a*) The apparent values of γ measured first with a bright and then with a blackened wire give rise to an additive correction There seems to be no doubt as to the magnitude of this correction in the case of air at room temperature as several observers have obtained closely agreeing values The value taken is 0 0021 Lummer and Pringsheim (2) added this amount to their experimental values for air hydrogen etc and Partington and Howe (3) apply the correction in the same way I have given reasons for assuming that the correction is not a pure radiation effect and it should vary in the inverse ratio of the thermal conductivity of the gas surrounding the thermometer wire For hydrogen the correction is then lowered to 0 0004 (1)

Since the publication of my paper Mandell (4) has shown that fine wire thermocouples record temperatures which depend amongst other factors on the nature of the surrounding gas The ratio of the differences found in air and in hydrogen is about 5 as I had assumed

The radiation correction in the case of nitrogen is the same as for air i e 0 0021 at room temperature The values at lower temperatures have been calculated by the application of Stefan s law

(*b*) Equation A (p 125) applies only to perfect gases which obey the law

Summary

Final Values for the Ratios of the Specific Heats of Nitrogen

Temp ° C	γ	Radiation correction r	$\gamma_1 = \gamma + r$	Thermodynamical correction factor $(1+f)$	Final values of γ	Values obtained by other Observers
10	1 4019	0 0021	1 4040	1 0010 (B) (C)	1 4054	1 4045 P & H (20°C) 1 406 D G & P(0°C)
− 78	1 4056	0 0005	1 4061	1 0030 (B) (C)	1 4103	
− 183	1 4158	—	1 4158	1 0310 (B) 1 0208 (C)	1 4596 1 4454	1 447 V (190° C)

P & H reference 3
D G & P 8
V 9

$pv = R\theta$ By assuming one of the many characteristic gas equations, it can be shown that γ must be multiplied by a factor $(1+f)$ in order to correct for the difference between the properties of the gas in question and those of a perfect gas

I have given the corrections calculated by using the gas equations proposed by Callendar (C) (5) and Berthelot (B) (6) as the difference in the magnitudes of these corrections is large at very low temperatures The constants used in calculating the Callendar correction are those given by Prof Callendar in his paper on the Thermodynamical Correction of the Gas Thermometer' For nitrogen the critical pressure is 33 atmos and the critical temperature 126 5° Abs

Accuracy of the Measurements

The effect of observational errors on the values of γ_e was considered in my previous paper In all the experiments by this method as is shown by illustrative tables of reduced observations both in this and in my earlier paper the maximum deviation of an individual from the mean result obtained with any one vessel at any one temperature is of the order 0 002 to 0 003 These differences are not greater than those found in the results of all other observers

Accuracy of the Extrapolation

Previous evidence of the parallelism of the linear relationships between γ_e and the reciprocal cube root of the volume of the vessel is confirmed by these experiments As it is shown that this linear relation holds over a considerable range in the size of the vessel used the accuracy of the extrapolated value γ will be of the same order as that of the individual means *

Recent Work by Other Observers

References to earlier measurements of the ratio of the specific heats of nitrogen will be found in the appended list of papers Partington and Howe measured the value of γ for nitrogen using a 60 litre vessel and a compensated thermometer of platinum wire 0 01 mm. in diameter An Einthoven string galvanometer was employed They found it necessary to make a somewhat provisional, but relatively large correction of about 1/2 per cent in order to correct for the so-called lag of their compensated thermometer The data for this correction were obtained from measurements made with uncompensated wires surrounded by air only I have previously pointed out that the application of the full correction calculated from these data is not justifiable *

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* The proper interpretation of my results for hydrogen at room temperature which is in accordance with all the experimental evidence indicates that my value of γ for hydrogen is correct to within 0 002 and not only within 0 012 as is suggested by Partington and Howe (7)

The excellent series of measurements by Dixon and his collaborators (8) at temperatures above that of the room and Valentiner's (9) measurement at about 82 5° Abs are especially valuable Dixon Campbell and Parker made direct measurements of the velocity of sound in nitrogen My measurement at room temperature is in excellent agreement with that deduced from their observations Valentiner used the Kundt's tube method and obtained the value 1 447 at about − 190° C

The values of the molecular specific heats at constant pressure and at constant volume can be calculated from the final values of those given above The specific heat values given in the following table have been calculated by using (B) Berthelot's and (C) Callendar's gas equations The gas constant has been taken as 1 985 and the molecular weight of nitrogen as 28 02

NITROGEN

Values of the Specific Heats

θ A	γ 1	S S_v	S_v	s_p	Direct measurements of s_p
283	0 4054	1 985	4 9	0 468	0 492 S & H 0 24 *
195	0 4103	14	4 910	0 2471	
90	0 4596 (B) 0 4454 (C)	2 02 (B) 2 189 (C)	4 968 (B) 4 914 (C)	0 2597 0 2535	0 2556 S & H 0 250*

* By linear extrapolation of Scheel and Heuse's experimental results, reference 10

The only direct observation of the specific heat of nitrogen at constant pressure and at the temperature of liquid air is that of Scheel and Heuse (10) The value of the ratio deduced from their measurements using Berthelot's equation is 1 468 Scheel and Heuse point out that when their results are calculated using the gas equation employed by Valentiner their value of γ is reduced to 1 459 which is about 1 per cent in excess of Valentiner s estimation of this quantity

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* The applicability of the full correction to their experiments on hydrogen is still more doubtful as any thermometric effect giving rise to such a correction would depend on the nature of the gas surrounding the thermometer wire Therefore it seems probable that Partington and Howe's value of γ for hydrogen, which, when corrected for radiation by the method I have adopted would be 1 4096, is somewhat too high My own value is 1 4070

The characteristic equation used by Valentiner was one deduced by Bestelmeyer and himself (11) as the result of an experimental study of the behaviour of nitrogen at liquid-air temperatures

It is interesting to note the excellent agreement between Valentiner s value for γ and my own when the latter is calculated by the aid of Callendar s equation As the Bestelmeyer and Valentiner relation represents the actual properties of nitrogen over a small range of temperature in the neighbourhood of − 190° C this agreement shows that Callendar s type of equation in addition to its precision at higher temperatures certainly represents the properties of nitrogen near its saturation point with greater exactitude than does that proposed by Berthelot

I have previously pointed out that the extrapolations in Scheel and Heuse s experiments may be somewhat doubtful (1) This is more especially the case in their experiments on nitrogen as flows of two widely differing values were used only

My value for the specific heat of nitrogen at constant pressure and at − 183° C is within 0 3 per cent. of the mean of the value they deduce and that obtained viz 0 250 by a linear extrapolation of their results

Variation of Molecular Specific Heat with Temperature

Dixon (8b) gives S_v 4 922 + 0 00041 t as representing the results of the experiments on nitrogen at atmospheric pressure and between 0° and 1000° C At high temperatures $S_p - S_v = 1\ 985$ so that $S_p = 6\ 91 + 0\ 00041\,t$ Callendar (5) has shown that his equation gives the relation $S_p = S_o +$ $an(n+1)\,cp/\theta$ where S_o is the limiting value of S_p at zero pressure and temperature θ

Callendar assumes that in this ideally rarefied condition the gas is perfect and S_o is independent of the temperature If the equation representing Dixon s experimental results is combined with Callendar s theoretical expression, in which the term involving $p/\theta^{2\cdot5}$ is negligible at high temperatures we may imagine Dixon s linear variation of S_p to hold for the zero pressure condition and 6 91 becomes the value of S_o at 0° C The molecular specific heats may then be calculated over the complete range of temperatures and pressures

The agreement with my experimental measurements at atmospheric pressure is very good as is shown in the adjoining table —

Temp t° C	S_p (exp)	S_p (calc)
10	6 92	6 92
78	6 92	6 91
183	7 10	7 07

NOTE —In referring to a criticism in my former paper Partington and Howe (7) say Brinkworth is therefore in error in stating that an emergent stem correction was applied in these experiments My statement referred explicitly (pp 539–540) to the value 1 4001 (air) obtained by Partington (12)

In an example which Partington gives in detail and which constitutes one of the individual experiments leading to this value the emergent stem correction is given as 0 01 C The paragraph from which they quote contained no reference to experiments made by them conjointly

REFERENCES

(1) Brinkworth Roy Soc Proc A vol 107 p 510 (1925)
(2) Lummer and Pringsheim Smith Contr (1898)
(3) Partington and Howe Roy Soc Proc A vol 105 p 225 (1924)
(4) Mandell Proc Phys Soc vol 38 p 47 (1925)
(5) Callendar Phil Mag vol 5 p 48 (1903)
(6) Berthelot Arch Néer vol 5 p 417 (1900)
(7) Partington and Howe, Roy Soc Proc A, vol 109, p 286 (1925)
(8) (a) Dixon Campbell and Parker Roy Soc Proc A vol 100 p 1 (1921) *see also*
    (b) Dixon and Greenwood Roy Soc Proc *A vol* 105 p 199 (1924)
(9) Valentiner Ann d Phys vol 15 p 74 (1904)
(10) Scheel and Heuse Ann d Phys vol 40 p 473 (1913)
(11) Valentiner and Bestelmeyer Ann d Phys vol 15 p 61 (1904)
(12) Partington, Roy Soc Proc A vol 100 p 27 (1921)

Adsorption Experiments with Radium D and Radium E

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Our knowledge of the behaviour of radio-elements in precipitation reactions is mainly due to Fajans and his co-workers,[*] who investigated the relation existing between the completeness of the removal of the radio-element from solution and the solubility of its salt They found that, when a filterable quantity of the precipitate of a common element was brought down in a solution containing an infinitesimal quantity of a radio-element, the radio-element itself was precipitated, if its corresponding compound was also insoluble This general conclusion was later investigated by Fajans and Richter (*loc cit*) with respect to thorium B, and it was further established that the degree of removal of the radio-element was dependent on the solubility of the precipitate of the ordinary element Thus with very insoluble precipitates such as bismuth sulphide and barium sulphate, thorium B was completely precipitated, while less insoluble precipitates like silver chloride carried down only part of the radio-element It was also suggested that when the precipitate was the insoluble salt of an isotope, the removal of the radio-element was to be ascribed to its solid solution in the isotopic precipitate, whereas removal by precipitates of dissimilar elements was an adsorption effect.

This last fact, the connection between the adsorption of radio-elements by various substances and the solubility of the corresponding active compounds, was the subject of detailed researches by Paneth,[†] and by Horovitz and Paneth.[‡] As a result, it was proved that the connection between the magnitude of the completeness of removal of the radio-element and the solubility of the analogous radio-active compound, held for a solid precipitate added to the solution as well as for the case of a precipitate brought down in the solution. Experiments have also been conducted in this field by Ebler and van Rhyn[§] and others

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[*] 'Ber. deutsch. chem Ges ,' vol 46, p 3486 (1913); *ibid* , vol 48, p. 700 (1915).

[†] 'Physikal Zeitschr.,' vol. 15, p 924 (1914)

[‡] 'Zeitschr Physikal. Chem ,' vol. 89, p. 513 (1915).

[§] 'Ber deutsch. chem Ges ,' vol 54, B, p 2896 (1921).

The general conclusions arrived at may be summarised as follows —

1 When radio elements are precipitated along with other precipitates the solubility product of the active ions present need not be attained before precipitation takes place

2 A radio-element will be removed by adsorption on a given adsorbent for which the analogous radio active compound (that is the compound of the radio element containing the same electronegative constituent as the adsorbent) is relatively insoluble and the less soluble the precipitate the more completely will the active element be removed

The object of the experiments to be described was to investigate how far these facts are applicable to two radio elements when these exist together in solution in radio active equilibrium and in particular to discover if removal by an isotopic adsorbent was more complete than that by a compound of like solubility of a dissimilar element In the course of the work results have been obtained which indicate that the half life period of radium E has a value slightly lower than that usually ascribed to it

The source of the radium D and radium E was a quantity of radon tubes, which had been used in medical treatment several years ago From these the later disintegration products of the radium series radium D radium E and radium F were removed by boiling the tubes in aqua regia evaporating the solution so obtained to small bulk adding more nitric acid evaporating almost to dryness and adding distilled water When a neutral solution was required the evaporation was continued to dryness and the active products dissolved in distilled water

The various precipitates formed in the active solution or the solids added to the solution were allowed time in every case to come into adsorptive equilibrium with the radio elements present Filtration was performed in a Buchner funnel and the activated precipitates measured on the filter papers but before filtering, the supernatant liquid was decanted to prevent any adsorption of the radio elements by the filter paper,* and the precipitates were washed by decantation The measurements of activity were made with a beta ray electroscope through a screen of gold beater s skin and two centimetres of air, so as to cut off all the alpha-radiation due to radium F The experiments are therefore concerned only with radium D and radium E which are isotopic with lead and bismuth respectively The activities are expressed in arbitrary units namely divisions of electroscope scale per minute

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* *cf* Godlewski, Phil. Mag., vol 27, p. 618 (1914)

1 *Adsorption by Sulphides*

(*a*) ***By Precipitation in Acid Solution***—Various sulphides were precipitated by passing sulphuretted hydrogen for 5 minutes through acid solutions (0 02 N) of the radio-elements containing quantities of the several salts so as to give the same mass of sulphide precipitate in each case which was just sufficient to form a very fine film on the filter paper Several parallel experiments were performed with similar results to those shown

Table I

Precipitate	Initial activity	Final activity
Lead sulphide	106	106
Bismuth sulphide	110	110
Mercuric sulphide	109	109
Copper sulphide	93	74 after 35 days
Ferrous sulphide (in neutral solution)	93	93

The same quantity of the active solution as used in above series without the addition of any other substance was evaporated to dryness on a watch glass and gave an activity of 111 and it is therefore apparent that radium D and radium F present together in equilibrium proportions can be completely removed by precipitation along with other substances Since the mercuric sulphide precipitate was as active as either that of lead sulphide or bismuth sulphide it appears that isotopic precipitates have no greater adsorptive power since certain non isotopic precipitates can completely carry down the radio active matter It will also be noted that the isotopic precipitate exhibits no preference in adsorption for its own isotope as compared with the other radio element All the above precipitates contain radium D and radium E in equilibrium except copper sulphide which has precipitated radium E in excess of its equilibrium quantity of radium D so that the activity declines till after 35 days or so equilibrium is established between the two radio elements The result obtained with copper sulphide would therefore appear to be an abnormal effect since there seems to be no reason why the copper sulphide should prefer the active isotope of bismuth to the active isotope of lead Fajans and Beer* found in the course of their experiments that abnormal adsorption did not interfere to any great degree but the anomalous result obtained above suggests that in the case of the simultaneous precipitation of two radio elements there may be abnormalities not apparent when dealing with the solution of a single radio-element

(*b*) ***Addition of Sulphides to Active Solution***—Table II shows the results obtained when sulphides were added to the acid active solution Sulphides of mercury (-ic) lead bismuth and copper were finely powdered and added to the same volume of active solution which had the same total activity, 111 as in Table I The mixture was shaken briskly for ten minutes and the activated sulphides measured on a filter paper as before parallel experiments being conducted

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* *Loc. cit.*

Table II

Precipitate	Initial activity	Final activity	Percentage of Radium D Removed
Lead sulphide	103	83	About 75 per cent
Bismuth sulphide	61	76	70
Mercuric sulphide	73	38	35
Copper sulphide	31	64	60

It is to be noted in these experiments where two radio elements are present in equilibrium solution that there is a very marked difference between the degree of adsorption taking place during precipitation and that occurring on a solid precipitate since in the first case all the radium D and its equilibrium quantity of radium E could be removed but in the second not more than 75 per cent The preference shown by copper sulphide in Table I for one of the radio elements is here proved to hold for all the sulphides when these are shaken up with the active solution instead of being precipitated in the solution Lead sulphide and bismuth sulphide for example when formed in the solution carry down all the radium D and radium E present but when these sulphides are added to the solution the lead sulphide adsorbs radium E in greater quantity than its equilibrium quantity of radium D and bismuth sulphide adsorbs radium D in greater quantity than its equilibrium amount of radium E Mercuric sulphide has a preferential adsorptive power for radium E and copper sulphide for radium D The smaller degree of removal in this set of experiments is understandable on the basis of the smaller specific surface available for adsorption in the case of a solid added to the solution as compared with a precipitate actually brought down in the solution But the selective action displayed as between the two radio elements present is not readily explained

2 *Adsorption by Chlorides*

(a) ***Precipitation by Hydrochloric Acid*** —The chlorides of lead silver and mercury (-ous) were precipitated with hydrochloric acid by adding it in excess to active solutions containing lead nitrate silver nitrate and mercurous nitrate respectively The very marked differences in the activities of these three precipitates is apparent in the curves shown in fig 1, which have been drawn from the following measurements The total activity was 72 in this series of experiments and also for those detailed in Tables IV and V

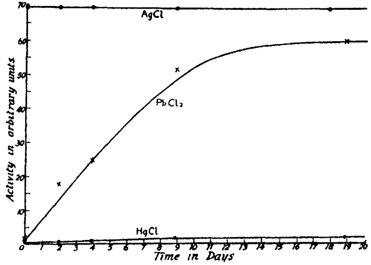

Fig 1 Activities of Chlorides precipitated in Acid Solution

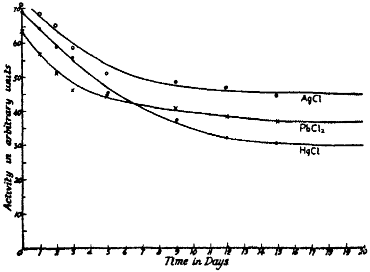

Fig 2.—Activities of Chlorides precipitated in Neutral Solution.

Table III

Time	Lead chloride precipitate	Silver chloride precipitate	Mercurous chloride precipitate
2 p.m. August 17	1 8	69 9	0 4
1 p.m , August 19	18 0	69 5	0 9
12 noon, August 21	24 5	70 0	1 0
12 noon, August 26	51 5	70 0	2 0
12 noon, September 5	60 0	69 4	2 1
5 p m , September 18	64 8	69 8	2 2
5 p.m September 21	65 7	69 8 thereafter constant	2 3

It will be observed that the lead chloride precipitate has a small initial activity, which gradually increases due to growth of radium E, and therefore, it may be said that lead chloride adsorbs practically only radium D, but this very completely which might be expected since the chloride of radium E, like the chloride of bismuth, is soluble in hydrochloric acid The silver chloride precipitate removes all the activity since in hydrochloric acid solution the solubility is very slight In neutral solution Fajans and Richter* found that silver chloride carried down only some 40 per cent of thorium B so that the connection between the degree of removal and the solubility of the precipitate holds very clearly in this case But that this is not the only factor involved is indicated by the fact that the mercurous chloride brings down very little of the active elements at all

(*b*) *Precipitation by Sodium Chloride Solution* —The influence of acidity in the degree of adsorption is shown by a comparison of fig 1 and fig 2, which latter shows the curves of activity of the same chlorides precipitated in neutral solution by sodium chloride solution Table IV gives the activities

Table IV

Time	Lead chloride precipitate	Silver chloride precipitate	Mercurous chloride precipitate
3 p.m , August 5	64 0	71 1	69 1
2 p.m , August 6	56 5	68 5	64 4
2 p.m., August 7	50 7	65 7	58 7
12 p.m., August 8	46 2	58 0	35 5
4 p.m., August 10	44 7	50 9	45 3
4 p.m., August 14	40 5	48 4	37 1
3 p.m., August 17	38 2	46 5	31 9
12 p.m., August 20	36 7	43 5	30 2
12 p.m., August 26	34 9	42 4	26 1
6 p.m., September 16	32 1	39 7 thereafter constant	23 1

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* *Loc. cit*

These readings indicate that the degree of adsorption by different precipitates is greatly affected by the acidity of the solution as was noted previously by Horovitz and Paneth * with respect to solutions of a single radio-element In general, radium D is more readily adsorbed in acid solution and radium E in neutral solution which is in keeping with the known facts of the partial solubility in water of the chloride of radium D and the solubility of that of radium E in hydrochloric acid solution since these chlorides are isotopic with those of lead and bismuth respectively But there is no obvious explanation of the poor adsorption obtained by the mercurous chloride precipitate in Table III Accordingly it has to be remarked that in the case of chloride precipitates as well as of sulphide precipitates certain abnormalities in adsorption are apparent The fact that an isotopic chloride has no unique powers of adsorption is to be deduced from the results shown

3 *Adsorption by Barium Sulphate precipitated in Solution*

The strong adsorptive powers of barium sulphate have been emphasized by Weiser and Sherrick † and this substance has been previously used to adsorb radio-elements In the present case it was desired to test further the main fact emerging from Sections 1 and 2 namely that an isotopic precipitate has no special adsorptive powers as compared with certain non isotopic precipitates and a sulphate precipitate is a most convenient one to employ, since lead sulphate isotopic with the sulphate of radium D is also insoluble in neutral or dilute acid solution To equal volumes of the same neutral solution of radium D and radium E solutions were added as shown and the activities of the resulting precipitates determined

Table V

To neutral solution of radium D and radium E added.	Initial activity	Final activity (after 35 days)
1 Barium nitrate and sodium sulphate	65	65
2 Barium nitrate and excess sulphuric acid	65	65
3 Barium nitrate and sodium sulphate in faintly alkaline solution	72	72
4 Barium nitrate lead nitrate and sodium sulphate	69	69
5 Lead nitrate and sodium sulphate	70	70
6 Lead nitrate and excess sulphuric acid	22	68

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* *Loc cit*

† Journ Phys Chem, vol 23, p 205 (1919)

These results show very clearly that the activity of the isotopic precipitate (lead sulphate) is no greater than that of the non-isotopic precipitate (barium sulphate) The influence of sulphuric acid in increasing the total adsorption (as noted by Horovitz and Paneth) is not apparent But it will be noted that, when barium sulphate is precipitated by sulphuric acid in excess, radium D and radium E are completely adsorbed, although the sulphate of radium E, like bismuth sulphate, is soluble in sulphuric acid solution , if, however, lead sulphate is precipitated by sulphuric acid in excess, radium D is removed in excess of its equilibrium quantity of radium E A precisely similar fact is observable in the chloride precipitations , and only in this case does the isotopic precipitate appear to possess any preferential powers

4 *Other Adsorptions*

(*a*) ***By Calcium Carbonate***—Calcium carbonate was precipitated with calcium chloride and sodium carbonate in a quantity of the active solution , and also along with basic lead carbonate in a similar quantity of solution In both cases radium D and radium E were completely removed, the presence of the carbonate of lead, isotopic with radium D, not affecting either the degree of adsorption or the ratio of D to E removed in any way

(*b*) ***By Ferric Hydroxide***—Ferric hydroxide precipitated in an active solution brought down all the active matter It has been noted* that ferric hydroxide adsorbs radium B and radium C, and also thorium B and thorium C in different proportions depending on the degree of acidity of the original solutions , and the effect is ascribed to the passing of the radioactive matter from the ionic to the colloidal state, the change being governed by the acidity of the solution In the case of solutions of radium D and radium E varying in acidity from 0 0005 N to 0 01 N, no variation in the ratio of radium D to radium E was found, both elements being completely removed On the basis of the colloidal theory advanced by Cranston, one may conclude that in such acid solutions radium D and radium E are present completely in the ionic condition, which agrees with the crystalloidal condition as previously determined for them by Paneth on the basis of dialysis experiments †

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* Cranston and Burnett, 'Journ Chem Soc ,' vol 119, p 2036 (1921), and Cranston and Hutton, *ibid.*, vol 121, p. 2843 (1922), and *ibid.*, vol 123, p. 1318 (1923)

† 'Kolloid Zeitschr.,' vol. 12, p 1 (1913).

5 *Determination of the Half life Period of Radium E by adsorption on Blood Charcoal*

Specially purified blood charcoal thoroughly shaken up with the active solution adsorbed all the radium E but only about 70 per cent of radium D The ratio of radium D adsorbed to radium E adsorbed seems to bear no relation to the relative quantities of these radio-elements present in the solution In this case there is no similarity between the adsorbed matter and the adsorbent and the radio elements are present in the form of soluble nitrates so that the effect is a true adsorption one without the complication of any precipitation phenomena This apparently selective adsorptive action of blood charcoal is being investigated with respect to solutions of radium D and radium E in various solvents

If to the active solution a quantity of lead as nitrate be first added and the adsorption on blood charcoal determined practically only radium E will be adsorbed since the infinitesimal quantity of radium D in the solution will have to compete for adsorption with the comparatively very large quantity of its isotope lead This experiment was repeated several times from 1 to 10 grams of lead nitrate being added in different tests and the activity on the filter paper was found to decay in every case practically to zero which indicates that radium E alone was present to the degree of accuracy of measurement claimed viz ½ per cent In this way a redetermination has been made of the half life period of radium E in view of the fact that Bastings value 4 98 days * suggested that the original value of 5 days as determined by Antonoff† and others was more accurate than the lower value of 4 85 days as advanced later by Thaller ‡ Details are given in Table VI of two of the four determinations made all of which gave 4 9 days as the period to an accuracy of 1 in 200 Column A in each case shows the activity obtained by measurement, while column B gives the theoretical numbers obtained by calculation on the basis of a half life period of 4 9 days

The experimental values and the theoretical numbers calculated on a basis of 4 9 days as the half life period are in good agreement The result confirms Thaller's value, further confirmation of which has been obtained recently by Fournier who gives the value 4 86 days in a paper§ published several months after the above experiments were performed

* 'Phil Mag.' vol 48, p 1075 (1924)
† 'Phil. Mag,' vol 19, p. 825 (1910)
‡ 'Wien Ber,' vol 121 p. 1611 (1912)
§ 'Compt Rend.,' vol. 181, p. 502 (1925)

Table VI

I			II		
Time in days.	Activity in Arbitrary Units		Time in days	Activity in Arbitrary Units.	
	A Experimental	B Theoretical for Radium E with period 4 9 days		A Experimental	B Theoretical for Radium E with period 4 9 days
0 0	77 3	77 3	0 0	49 0	49 0
2 0	60 0	58 3	1 0	42 8	42 6
2 96	53 4	50 9	2 0	36 6	36 9
4 04	43 6	43 7	3 04	32 3	31 9
4 875	38 9	38 8	3 96	29 2	28 0
7 04	28 6	28 6	5 08	23 8	23 9
9 04	23 1	21 7	6 125	20 5	20 6
20 0	5 5	4 6	13 04	8 5	7 7
25 79	3 6	2 0	22 96	2 1	1 9
69 0	0 2	1	73 0	nil	nil

Synopsis

The results enumerated in this paper may be summarised as follows —

(1) Previously known facts regarding the adsorption of a single radio element from its solution either by a precipitate formed in the solution or by an added solid are in general found to hold for the simultaneous adsorption of the two radio-elements radium D and radium E when present in radio active equilibrium But it is pointed out that the results in several cases are influenced by abnormal adsorption effects

(2) Isotopic precipitates possess no greater adsorptive powers than certain non isotopic precipitates which can completely carry down the radio-elements

(3) But an isotopic precipitate formed under such conditions that one of the two analogous radio active compounds is soluble, exhibits a preference for its own isotope, whereas a non isotopic precipitate displays no such preference

(4) The addition of a soluble lead salt to a solution of radium D and radium E stops the adsorption of radium D by charcoal, and in this way radium E has been extracted in a state of great purity

(5) The half life period of radium E has been so determined as 4 9 days

The Elastic Stability of a Corrugated Plate

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1 *Introduction and Summary* This paper deals with the elastic stability of a corrugated plate under thrust along its generators Besides the assumption common to all such problems that the plate is thin it is supposed that the depth of a bay (d fig 1) is a small multiple of h the semi thickness and that the transverse expansion that is the usual accompaniment of a longitudinal thrust is prevented by a thrust in a perpendicular direction The equations derived in §§ 2 7 are then soluble and the critical stress in any case can be found from an equation expressing that an infinite determinant is zero

The numerical work that has been done has been limited to the two cases in which $d = 10h$ and $d = 5h$ respectively As a preliminary in §§ 8 11 it has been supposed that σ Poisson s ratio is zero The equations are greatly simplified by this supposition and results can easily be obtained which are a valuable guide to the more complicated arithmetic of the normal case in which σ does not vanish In particular this preliminary work is used to find the favourite type of distortion (that possible under the least stress) in the other case it can be seen that the favourite types are the same whether σ is or is not zero The necessary exploration is therefore done for $\sigma = 0$ and the arithmetic in the more practical case in which we suppose that $\sigma = \frac{1}{4}$ is confined to the calculation of stresses causing definite modes of distortion

For $\sigma = \frac{1}{4}$ numerical results are given in §§ 12–14 and shown in figs 3 and 4 It is found in the cases considered that the ratio of length of bay (l) to height (H) should not exceed $\frac{1}{4}$ if the critical stress is to be as large as possible The critical stress in a corrugated plate can be conveniently stated by giving its ratio to that in a plane plate of the same thickness and height If $l/H < \frac{1}{4}$ this ratio is about 30 when $d = 5h$ and over 130 when $d = 10h$ This may be stated in different terms in a manner that has an application more direct to practical problems Two plates of equal thickness and height will weigh the same if they are of the same length and of the same material If one is plane and the other corrugated so that $d = 10h$ and $l/H < \frac{1}{4}$ the latter though weighing the same will take over 130 times the total load of the other The possible application of this work is to the use in aeroplane construction of corrugated plates which must be light and yet take considerable loads The possibility of extending this work to plates with deeper bays is considered in §15 this extension is necessary in deciding what is the greatest value of d/h to which the approximate solution of this paper will apply It does not appear worth while to attempt this until some experimental results are available For the same reason the form of the surface of the plate after collapse has taken place has not been considered numerically though in § 16 the general nature of the favourite types of distortion is stated

The writer is greatly indebted to Prof G I Taylor at whose suggestion this problem was attacked and to Mr R V Southwell for his valuable criticism and advice

§ 2 The position of P any point of the middle surface of the plate is specified by α, the distance of P measured along a generator from an arbitrary line of curvature and by β the distance of P measured along a line of curvature from a generator ρ the radius of curvature of the section of the surface by a plane perpendicular to the generators is a function of β only and we write

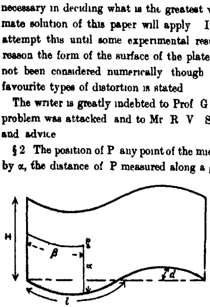

Fig. 1

$$1/\rho = c \sin n\beta \qquad (1)$$

where c and n are constants c being the maximum curvature

Given c and n equation (1) defines the middle surface but a more convenient description of a corrugated plate can be given in terms of four lengths H the height h, the semi thickness of the material of the plate l the length of a bay of the middle surface and d the depth of a bay (fig 1)

The fundamental assumptions made in what follows are that the ratio h/H is small and that d is comparable with h The first of these is of course inevitable instability is only of practical interest and is only calculable if the plate considered is thin Little progress has been made without some such assumption as the second whose limitations are discussed later in § 15. The numerical work has been confined to the two cases in which $d = 10h$ and $d = 5h$ respectively so that we take d to be of the order of h throughout.

The four lengths and the quantities c and n of (1) are naturally not independent Clearly $l = \pi/n$ while

$$d = \int_0^{\pi/2n} \sin\left(\frac{c}{n}\cos n\beta\right) d\beta$$

$$= \frac{c}{n^2}\left[1 - \frac{2}{3\ 3!}\left(\frac{c}{n}\right)^2 + \quad\right]$$

This can be written

$$c = dn^2 \tag{2}$$

if it is assumed that c/n which is approximately equal to $\pi d/l$ is small This is supposed here but the restriction can probably be removed in most cases at the cost of slightly complicating the arithmetic it is necessary however that the plate should not be so rapidly corrugated that the maximum curvature is large in spite of the fact that d is small

§ 3 *The Shell Equations* We investigate the stability of the plate under thrust parallel to its generators it being supposed that the aggregate lateral expansion that would normally take place is prevented by suitable thrusts in a perpendicular direction Since d is not more than $10h$ in the cases to be considered numerically it may be assumed that the critical thrust is the same as that of a plane plate of the same height and of semi thickness some small multiple of h

The displacements of any point of the middle surface are written u v w u being the displacement along the generator v the perpendicular tangential displacement and w the normal displacement From the plane plate comparison above it follows that in the critical configuration u is of the order h^2 * while it can be seen *a posteriori* that v is also of order h^2 and w is of order h

The reason for the higher order of w is fairly clear physically To prevent lateral expansion a transverse thrust must be applied which in the case of a corrugated plate with a shallow bay may be expected to be roughly the longitudinal thrust multiplied by Poisson s ratio In the critical configuration there is accordingly a transverse thrust about one-quarter of the high collapsing thrust evidently a corrugated plate can offer but little resistance to such a stress and relatively high normal displacements ensue

Lastly from (2) $1/\rho$ is of the order of h Shell equations that are applicable with slight modification to this problem have been given by the writer in a recent paper † They need not be set down in full here as we immediately approximate to them by retaining in the first two equations the principal terms of which involve u and v linearly no terms of order higher than h^2 and in the third equation whose most important term is of order h^2w no terms of order higher than h^3 The equations are considerably simplified by this procedure and become

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* It is convenient to make some statements of this type in this section. The meaning is merely that u contains h^2 as a factor In the critical equilibrium of a plane plate $\partial u/\partial x$ is of the order $(h/H)^2$

† Roy Soc Proc., A, vol. 107 p. 734 (1925) By shell equations is meant equations in terms of the displacements of points of the middle surface only

$$\frac{\partial}{\partial\alpha}\left[\frac{\partial u}{\partial\alpha}+\tfrac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2+\sigma\left\{\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\tfrac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2\right\}\right]$$
$$+\frac{1-\sigma}{2}\frac{\partial}{\partial\beta}\left[\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}+\frac{\partial w}{\partial\alpha}\frac{\partial w}{\partial\beta}\right]=0 \qquad (3)$$

$$\frac{\partial}{\partial\beta}\left[\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\tfrac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2+\sigma\left\{\frac{\partial u}{\partial\alpha}+\tfrac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2\right\}\right]$$
$$+\frac{1-\sigma}{2}\frac{\partial}{\partial\alpha}\left[\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}+\frac{\partial w}{\partial\alpha}\frac{\partial w}{\partial\beta}\right]=0 \qquad (4)$$

and

$$\frac{h^2}{3}\nabla_1{}^4w-\frac{1}{\rho}\left[\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\tfrac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2+\sigma\left\{\frac{\partial u}{\partial\alpha}+\tfrac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2\right\}\right]$$
$$-\frac{\partial}{\partial\alpha}\left[\frac{\partial w}{\partial\alpha}\left\{\frac{\partial u}{\partial\alpha}+\sigma\left(\frac{\partial v}{\partial\beta}-\frac{w}{\rho}\right)\right\}\right]-\frac{\partial}{\partial\beta}\left[\frac{\partial w}{\partial\beta}\left\{\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\sigma\frac{\partial u}{\partial\alpha}\right\}\right]$$
$$-\frac{1-\sigma}{2}\frac{\partial}{\partial\alpha}\left[\frac{\partial w}{\partial\beta}\left(\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}\right)\right]-\frac{1-\sigma}{2}\frac{\partial}{\partial\beta}\left[\frac{\partial w}{\partial\alpha}\left(\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}\right)\right]=0 \qquad (5)$$

The equations from which (3) (4) and (5) have been deduced ignore all terms of the first order in u v w if multiplied by h^3 or higher power of h and all terms of the third and higher orders in u v w This approximation is sufficient so far as deducing terms of order h^2 in (3) and (4) is concerned but clearly there is no reason for excluding terms in w^3 from (5) The importance of such terms in the case of a plane plate when w is of the order h has been pointed out by J Prescott * and it happens that the terms that must be added to the left side of (5) are exactly the same as those shown to be necessary by him in the corresponding plane plate equation The reason is this the complete third order terms in (5) must contain those of the plane plate case which is reached by putting $1/\rho=0$ the other third-order terms must contain a positive integral power of $1/\rho$ as a factor † and hence must be of order higher than h^3 ‡

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* 'Phil. Mag., vol. 43 p 97 (1922)

† ρ only appears in this form in the equations

‡ An independent evaluation of such third-order terms as are required in this problem has been made on the lines of Section 5 of the paper by the writer quoted above that is to say, without appealing to results of the theory of thin shells There appears to be no point in setting out this work; the necessary terms may be found in equations (5) to (14) of Prescott's paper

The complete equations for this problem are now (3), (4) and

$$\begin{aligned}\frac{h^2}{3}\nabla_1{}^4 w-\frac{1}{\rho}\left[\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\frac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2+\sigma\left\{\frac{\partial u}{\partial\alpha}+\frac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2\right\}\right]\\ -\frac{\partial}{\partial\alpha}\left[\frac{\partial w}{\partial\alpha}\left\{\frac{\partial u}{\partial\alpha}+\frac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2+\sigma\left(\frac{\partial v}{\partial\beta}-\frac{w}{\rho}\right)+\frac{\sigma}{2}\left(\frac{\partial w}{\partial\beta}\right)^2\right\}\right]\\ -\frac{\partial}{\partial\beta}\left[\frac{\partial w}{\partial\beta}\left\{\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\frac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2+\sigma\frac{\partial u}{\partial\alpha}+\frac{\sigma}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2\right\}\right]\\ -\frac{1-\sigma}{2}\frac{\partial}{\partial\alpha}\left[\frac{\partial w}{\partial\beta}\left\{\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}+\frac{\partial w}{\partial\alpha}\frac{\partial w}{\partial\beta}\right\}\right]\\ -\frac{1-\sigma}{2}\frac{\partial}{\partial\beta}\left[\frac{\partial w}{\partial\alpha}\left\{\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}+\frac{\partial w}{\partial\alpha}\frac{\partial w}{\partial\beta}\right\}\right]=0 \qquad (6)\end{aligned}$$

§ 4 *The Equilibrium Configuration*.—Writing

$$T_1=\frac{\partial u}{\partial\alpha}+\frac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2+\sigma\left\{\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\frac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2\right\},$$

$$T_2=\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\frac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2+\sigma\left\{\frac{\partial u}{\partial\alpha}+\frac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2\right\},$$

and

$$S=\frac{1-\sigma}{2}\left\{\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}+\frac{\partial w}{\partial\alpha}\frac{\partial w}{\partial\beta}\right\},$$

equations (3), (4), and (6) become

$$\frac{\partial T_1}{\partial\alpha}+\frac{\partial S}{\partial\beta}=0, \qquad (7)$$

$$\frac{\partial T_2}{\partial\beta}+\frac{\partial S}{\partial\alpha}=0, \qquad (8)$$

and

$$\begin{aligned}\frac{h^2}{3}\nabla_1{}^4 w-\frac{T_2}{\rho}-\frac{\partial}{\partial\alpha}\left(T_1\frac{\partial w}{\partial\alpha}\right)-\frac{\partial}{\partial\beta}\left(T_2\frac{\partial w}{\partial\beta}\right)\\ -\frac{\partial}{\partial\alpha}\left(S\frac{\partial w}{\partial\beta}\right)-\frac{\partial}{\partial\beta}\left(S\frac{\partial w}{\partial\alpha}\right)=0\end{aligned}$$

The last of these can be simplified by the use of (7) and (8) to the form

$$\frac{h^2}{3}\nabla_1{}^4 w-\frac{T_2}{\rho}-T_1\frac{\partial^2 w}{\partial\alpha^2}-T_2\frac{\partial^2 w}{\partial\beta^2}-2S\frac{\partial^2 w}{\partial\alpha\partial\beta}=0 \qquad (9)$$

The equations can be solved by

$$T_1=C_1,\quad T_2=C_2,\quad S=0,$$

where C_1 and C_2 are constants, provided that

$$\frac{h^2}{3}\nabla_1^4 w - \frac{C_2}{\rho} - C_1\frac{\partial^2 w}{\partial\alpha^2} - C_2\frac{\partial^2 w}{\partial\beta^2} = 0 \tag{10}$$

$$\frac{\partial u}{\partial\alpha} + \frac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2 + \sigma\left\{\frac{\partial v}{\partial\beta} - \frac{w}{\rho} + \frac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2\right\} = C_1 \tag{11}$$

$$\frac{\partial v}{\partial\beta} - \frac{w}{\rho} + \frac{1}{2}\left(\frac{\partial w}{\partial\beta}\right)^2 + \sigma\left\{\frac{\partial u}{\partial\alpha} + \frac{1}{2}\left(\frac{\partial w}{\partial\alpha}\right)^2\right\} = C_2 \tag{12}$$

and

$$\frac{\partial v}{\partial\alpha} + \frac{\partial u}{\partial\beta} + \frac{\partial w}{\partial\alpha}\frac{\partial w}{\partial\beta} = 0 \tag{13}$$

Setting $u = A\alpha$ A constant and supposing that v and w are independent of α equations (10) (11) and (12) become

$$\frac{h^2}{3}\frac{d^4 w}{d\beta^4} - \frac{C_2}{\rho} - C_2\frac{d^2 w}{d\beta^2} = 0 \tag{14}$$

$$A = \frac{C_1 - \sigma C_2}{1 - \sigma^2} \tag{15}$$

and

$$\frac{dv}{d\beta} - \frac{w}{\rho} + \frac{1}{2}\left(\frac{dw}{d\beta}\right)^2 = \frac{C_2 - \sigma C_1}{1 - \sigma^2} \tag{16}$$

while (13) is satisfied identically

Substituting the value of ρ given by (1) it is seen that

$$w = kc \sin n\beta \tag{17}$$

k constant will satisfy (14) provided

$$h^2 n^4 k/3 - (1 - kn^2)\, C_2 = 0 \tag{18}$$

From (16)

$$\frac{dv}{d\beta} = \frac{C_2 - \sigma C_1}{1 - \sigma^2} + kc^2 \sin^2 n\beta - \frac{k^2c^2n^2}{2}\cos^2 n\beta$$

$$= \frac{C_2 - \sigma C_1}{1 - \sigma^2} + kc^2/2 - k^2c^2n^2/4 - (kc^2/2 + k^2c^2n^2/4)\cos 2n\beta$$

As it is supposed that there is no aggregate lateral expansion of the plate $dv/d\beta$ must be periodic so that we must have

$$(C_2 - \sigma C_1)/(1 - \sigma^2) + kc^2/2 - k^2c^2n^2/4 = 0 \tag{19}$$

The expression for v is not wanted [*]

[*] This expression contains an arbitrary constant which properly should correspond to a rigid body displacement That v = const does not exactly represent such a displacement is due to the fact that the shell equations are only approximate As the plate is assumed shallow, the discrepancy is of minor importance. In any case, the constant can naturally be ignored

C_1 and C_2 are proportional to the applied thrusts along the generators and transversely, respectively Given C_1, C_2 and k can be found from (18) and (19), and A from (15), hence the values of u v and w That C_2 is known when C_1 is given is, of course a consequence of the restriction that there should be no lateral expansion The first part of the problem the determination of the equilibrium configuration of the plate under thrust, is therefore completed

§ 5 *The Stability Equations* If the equilibrium configuration u, v w, investigated above is critical there will be a neighbouring configuration of equilibrium which we write $u+u'$, $v+v'$, $w+w'$ The stability equations are derived by substituting first u v, w in the shell equations then $u+u'$, $v+v'$, $w+w'$, and finally subtracting the two sets of equations In the equations thus produced powers of u' v' and w' above the first can be ignored There results

$$\frac{\partial}{\partial\alpha}\left[\frac{\partial u'}{\partial\alpha}+\sigma\left\{\frac{\partial v'}{\partial\beta}-\frac{w}{\rho}+\frac{dw}{d\beta}\frac{\partial w}{\partial\beta}\right\}\right] \\ +\frac{1-\sigma}{2}\frac{\partial}{\partial\beta}\left[\frac{\partial v'}{\partial\alpha}+\frac{\partial u'}{\partial\beta}+\frac{dw}{d\beta}\frac{\partial w'}{\partial\alpha}\right]=0, \quad (20)$$

$$\frac{\partial}{\partial\beta}\left[\frac{\partial v}{\partial\beta}-\frac{w}{\rho}+\frac{dw}{d\beta}\frac{\partial w}{\partial\beta}+\sigma\frac{\partial u'}{\partial\alpha}\right] \\ +\frac{1-\sigma}{2}\frac{\partial}{\partial\alpha}\left[\frac{\partial v'}{\partial\alpha}+\frac{\partial u'}{\partial\beta}+\frac{dw}{d\beta}\frac{\partial w'}{\partial\alpha}\right]=0, \quad (21)$$

and

$$\frac{k^2}{3}\nabla_1{}^4w'-\left[\frac{1}{\rho}+\frac{d^2w}{d\beta^2}\right]\left[\frac{\partial v'}{\partial\beta}-\frac{w'}{\rho}+\frac{dw}{d\beta}\frac{\partial w'}{\partial\beta}+\sigma\frac{\partial u'}{\partial\alpha}\right] \\ -\frac{\partial^2w'}{\partial\alpha^2}\left[\frac{du}{d\alpha}+\sigma\left\{\frac{dv}{d\beta}-\frac{w}{\rho}+\tfrac{1}{2}\left(\frac{dw}{d\beta}\right)^2\right\}\right] \\ -\frac{\partial^2w'}{\partial\beta^2}\left[\frac{dv}{d\beta}-\frac{w}{\rho}+\tfrac{1}{2}\left(\frac{dw}{d\beta}\right)^2+\sigma\frac{du}{d\alpha}\right]=0$$

Using (15) and (16) the last of these becomes

$$\frac{k^2}{3}\nabla_1{}^4w'-\left[\frac{1}{\rho}+\frac{d^2w}{d\beta^2}\right]\left[\frac{\partial v'}{\partial\beta}-\frac{w'}{\rho}+\frac{dw}{d\beta}\frac{\partial w'}{\partial\beta}+\sigma\frac{\partial u'}{\partial\alpha}\right] \\ -C_1\frac{\partial^2w'}{\partial\alpha^2}-C_2\frac{\partial^2w'}{\partial\beta^2}=0. \quad (22)$$

At this point it is convenient to state the mathematical problem in full, repeating some equations that have already been given We have to find the value of C_2 that leads to a non zero solution in u', v' and w' of (20), (21) and (22), where

$$1/\rho = w/k = c \sin n\beta, \tag{23}$$

$$h^2 n^4 k/3 - (1 - kn^2)\, C_2 = 0, \tag{24}$$

and

$$(C_2 - \sigma C_1)/(1 - \sigma^2) + kc^2/2 - k^2c^2n^2/4 = 0. \tag{25}$$

The next consideration is to put these equations in a form suitable for numerical work

§ 6 –The first stage in the manipulation is effectively equivalent to the elimination of one of the variables u', v', w' Setting

$$\frac{\partial u'}{\partial \alpha} + \sigma\left(\frac{\partial v'}{\partial \beta} - \frac{w'}{\rho} + \frac{dw}{d\beta}\frac{\partial w'}{\partial \beta}\right) = \frac{\partial^2 \psi}{\partial \beta^2}, \tag{26}$$

$$\frac{\partial v}{\partial \beta} - \frac{w'}{\rho} + \frac{dw}{d\beta}\frac{\partial w'}{\partial \beta} + \sigma\frac{\partial u'}{\partial \alpha} = \frac{\partial^2 \psi}{\partial \alpha^2}, \tag{27}$$

and

$$\frac{1-\sigma}{2}\left(\frac{\partial v'}{\partial \alpha} + \frac{\partial u}{\partial \beta} + \frac{dw}{d\beta}\frac{\partial w'}{\partial \alpha}\right) = -\frac{\partial^2 \psi}{\partial \alpha \partial \beta}, \tag{28}$$

equations (20) and (21) are satisfied,* while (22) becomes

$$\frac{h^2}{3}\nabla_1{}^4 w - \left(\frac{1}{\rho} + \frac{d^2 w}{d\beta^2}\right)\frac{\partial^2 \psi}{\partial \alpha^2} - C_1\frac{\partial^2 w'}{\partial \alpha^2} - C_2\frac{\partial^2 w'}{\partial \beta^2} = 0, \tag{29}$$

u' and v' can be eliminated from (26), (27) and (28), the result being

$$\nabla_1{}^4 \psi + (1 - \sigma^2)\left(\frac{1}{\rho} + \frac{d^2 w}{d\beta^2}\right)\frac{\partial^2 w'}{\partial \alpha^2} = 0 \tag{30}$$

A non zero solution in w and ψ of (29) and (30) evidently implies a non-zero solution in u', v' and w' of the stability equations As stated what has been done is effectively to eliminate one of the original variables the method adopted gives a more symmetrical form than would result from a direct attempt at elimination, and entails less labour

It may be noticed that if

$$\frac{1}{\rho} + \frac{d^2 w}{d\beta^2} = 0,$$

equation (29) reduces to the stability equation of a plane plate, this relation, in fact, evidently implies that in the equilibrium configuration the middle surface is straightened out However, from equation (24) an infinite transverse tension* is required for this, it is a familiar enough experience that it is exceedingly difficult to straighten by tension any naturally curved body, as, for instance, a coil of wire

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* This procedure is analogous to that commonly followed in two-dimensional problems. *Cf.* A. E. H. Love, 'Mathematical Theory of Elasticity' (3rd edition), § 144, also Prescott, *loc cit.*, p. 101.

§ 7 —The equations must now be put in non-dimensional form, (29) and (30) may be satisfied by

$$w = \mathrm{W} \sin \mu\alpha, \tag{31}$$

and

$$\psi = \psi_1 \sin \mu\alpha, \tag{32}$$

where μ is a constant, and W and ψ_1 are functions of β only Let the variable β be changed to $\theta\ (-\ n\beta)$ and let

$$\mathrm{C}_1 = \mathrm{C}_1\, h^2\mu^2 \qquad \mathrm{C}_2 - \mathrm{C}_2\, h^2\mu^2, \qquad \psi_1 = h\phi,$$

and

$$d/h = d\,, \quad \mu/n = \mu'$$

Equations (29) and (30) then become

$$\frac{d^4\mathrm{W}}{d\theta^4} - 2\mu^2 \frac{d^2\mathrm{W}}{d\theta^2} + \mu^4\,\mathrm{W} + 3\,\mathrm{C}_1'\,\mu'^4\,\mathrm{W} - 3\,\mathrm{C}_2'\mu'^2 \frac{d^2\mathrm{W}}{d\theta^2}$$
$$+ 3\,(1 - kn^2)\, d'\mu'^2 \sin\theta\,\phi = 0\,,$$

and

$$\frac{d^4\phi}{d\theta^4} - 2\mu'^2\,\frac{d^2\phi}{d\theta^2} + \mu'^4\phi - (1 - \sigma^2)\,(1 - kn^2)\, d'\mu'^2 \sin\theta\,\mathrm{W} = 0$$

Finally let $kn^2 = a$,

$$\mathrm{F} = 3\,(1 - a)\, d'\mu^2\,, \quad \mathrm{G} = (1 - \sigma^2)\,(1 - a)\, d'\mu'^2 \tag{33}$$

and

$$y = 3\,\mathrm{C}_1'\mu'^4, \quad z = 3\,\mathrm{C}_2'\mu^2 \tag{34}$$

The resulting equations are

$$\frac{d^4\mathrm{W}}{d\theta^4} - 2\mu'^2\frac{d^2\mathrm{W}}{d\theta^2} + \mu'^4\,\mathrm{W} + y\mathrm{W} - z\,\frac{d^2\mathrm{W}}{d\theta^2} + \mathrm{F}\sin\theta\,\phi = 0, \tag{35}$$

and

$$\frac{d^4\phi}{d\theta^4} - 2\mu'^2\,\frac{d^2\phi}{d\theta^2} + \mu'^4\,\phi - \mathrm{G}\sin\theta\,\mathrm{W} = 0, \tag{36}$$

while from (24) and (25)

$$z = a/(1 - a), \tag{37}$$

and

$$a\,[1 + 3\,(1 - \sigma^2)\, d'^2/2] = 3\sigma\,\mathrm{C}_1'\,\mu'^2 + 3\,(1 - \sigma^2)\, d'^2a^2/4 - a^2/(1 - a) \tag{38}$$

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* A tension because k must be positive in this case, k is always negative in the conditions considered here—a transverse *thrust* being, of course, necessary to prevent lateral expansion.

In the first case considered numerically we take $\sigma = 1/4$, $d' = 10$. The last equation is then

$$a = (0{\cdot}0052957)\, C_1'\mu'^2 + (0{\cdot}49647)\, a^2 - (0{\cdot}0070609)\, \frac{a^2}{1-a} \tag{39}$$

In the second case, the same value of σ is used, and $d' = 5$, so that

$$a = (0{\cdot}020743)\, C_1'\mu'^2 + (0{\cdot}48617)\, a^2 - (0{\cdot}027657)\, \frac{a^2}{1-a} \tag{40}$$

Equations (33) to (39) contain a complete statement of the problem, are non-dimensional, and are in the form that has been found most suitable for numerical work.

§ 8. *The Assumption* $\sigma = 0$. By analogy with other problems in elastic stability, we can suppose that the collapsing thrust in a corrugated plate is not importantly affected by the value of Poisson's ratio for the material. For instance, in the problem most resembling the present one that of the stability of a cylindrical shell under axial thrust, σ appears in the formula for the collapsing thrust solely in the usual factor $(1 - \sigma^2)$. Since for most materials σ is in the neighbourhood of $\frac{1}{4}$, the supposition that it is zero leads to an error in the determination of the critical thrust usually less than 10 per cent.

The numerical discussion of a problem of stability is necessarily lengthy, since the object is not merely to find the stress that will cause a given type of collapse, but also to find that type of collapse (the "favourite type of distortion") that takes place under the least stress. Inevitably, a considerable exploration is necessary. By assuming that $\sigma = 0$, a striking simplification of the equations results, and it is relatively easy to find the favourite type of distortion. We can then find the stress that will cause collapse of the *same type* when σ is not zero, and if there is a reasonable agreement between the two values it is natural to conclude that the favourite modes are the same in the two cases.* At the least, the numerical work in one case is an obviously valuable guide to that in the other.

The physical interpretation of the assumption $\sigma = 0$ is a simple one. It means that the sole effect of a longitudinal thrust is to compress the parallel filaments of the plate; the transverse expansion that normally accompanies such a compression does not take place and no perpendicular thrust is necessary to prevent lateral movement. As a consequence, in the equilibrium configuration $w = 0$, and there is no need for the third order terms that arise in the general case

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* The argument as stated here in general terms is not, of course, conclusive, but it is quite clear from numerical and other considerations that in the work below the favourite type when $\sigma \neq 0$ has, in fact, been obtained.

§ 9 *The Simplified Equations*—Putting $\sigma = 0$ in (38), we see that $a = 0$, from (37) $z = 0$; and

$$F = 3\,G = 3d'\,\mu'^2$$

If $x = d'\,\mu'^2$, equations (35) and (36) become

$$\frac{d^4W}{d\theta^4} - 2\mu'^2\frac{d^2W}{d\theta^2} + \mu'^4W + yW + 3x\sin\theta\,\phi = 0, \tag{41}$$

and

$$\frac{d^4\phi}{d\theta^4} - 2\mu'^2\frac{d^2\phi}{d\theta^2} + \mu'^4\phi - x\sin\theta\,W = 0 \tag{42}$$

d' $(= d/h)$ is known, assuming a value of μ', we have that of x, and have to find the least value of y that permits a non-zero solution in W and ϕ of (41) and (42)

§ 10 *Type Solutions*—The expressions

$$\left.\begin{aligned} W &= w_1\cos\lambda\theta + w_2\cos(2-\lambda)\,\theta + w_3\cos(2+\lambda)\,\theta \\ &\qquad + w_4\cos(4-\lambda)\,\theta + \\ \phi &= \phi_1\sin(1-\lambda)\,\theta + \phi_2\sin(1+\lambda)\,\theta + \phi_3\sin(3-\lambda)\,\theta \\ &\qquad + \phi_4\sin(3+\lambda)\,\theta + \end{aligned}\right\} \tag{43}$$

where $\lambda, w_1, w_2, \ldots, \phi_1, \phi_2, \ldots$ are constants, will satisfy (41) and (42) if certain relations hold between the coefficients. There is an infinity of such relations, which can be satisfied by non-zero constants if an infinite determinant vanishes This condition is

$$\begin{vmatrix} F(1-\lambda), & -\dfrac{x}{2}, & 0, & \dfrac{x}{2}, & 0, & . \\ \dfrac{3x}{2}, & F(\lambda)+y, & \dfrac{3x}{2}, & 0, & 0, & . \\ 0, & -\dfrac{x}{2}, & F(1+\lambda), & 0, & 0, & \\ -\dfrac{3x}{2}, & 0, & 0, & F(2-\lambda)+y, & \dfrac{3x}{2}, & \\ 0, & 0, & 0, & -\dfrac{x}{2}, & F(3-\lambda), & \end{vmatrix} = 0, \tag{44}$$

where $F(z) = (z^2 + \mu'^2)^2$.

That the determinant is convergent is evident upon dividing rows and columns by the appropriate factors. It can be written

$$\left|\begin{array}{lllll} \cdot & & & & \\ , & F(2n-1+\lambda), & 0, & 0, & \frac{x}{2}, \\ \cdot\,, & 0, & F(2n-\lambda)+y, & \frac{3x}{2}, & 0 \\ , & 0, & -\frac{x}{2}, & F(2n+1-\lambda), & 0, \\ , & -\frac{3x}{2}, & 0, & 0, & F(2n+\lambda)+y. \\ & & & & \end{array}\right|$$

Divide the first row and column written down by $(2n - 1 + \lambda)^2$, the second row and column by $(2n - \lambda)^2$, and so on. Typical diagonal terms are then

$$[1 + \mu'^2/(2n - \lambda)^2]^2 + y/(2n - \lambda)^4 \text{ and } [1 + \mu'^2/(2n - 1 + \lambda)^2]^2,$$

and typical non-diagonal terms,

$$3x/2\,(2n - \lambda)^2\,(2n + 1 - \lambda)^2 \text{ and } - x/2\,(2n - \lambda)^2\,(2\,n + 1 - \lambda)^2$$

Conditions sufficient for convergence are that the product of the diagonal terms should converge absolutely, and that the sum of the non-diagonal terms should converge absolutely[*] The product of the diagonal terms converges like the product $\Pi\,(1 + 1/n^2)$, the sum of the non-diagonal terms like the series $\Sigma\,1/n^4$, and consequently the determinant converges There is, of course, no need to divide the rows and columns in numerical work, and they are left as they stand in the case considered below, § 11

Given x, y can be determined from equation (44) for a given value of λ It is not necessary to consider all values of λ when finding the minimum value of y. Writing $\lambda = 2 + \lambda'$ in (43) the forms of W and ϕ are not altered, so that values of λ between 0 and 2 alone need be considered Again, putting first $\lambda = 1 + \lambda'$, and then $\lambda = 1 - \lambda'$, a pair of identical expressions for W and ϕ are obtained For given x, y is a function of λ[†], this function is periodic with period 2, and is symmetrical about the value $\lambda = 1$ It already appears probable that the minimum value of y is to be found when $\lambda = 0$ or when

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[*] Whittaker and Watson, 'Modern Analysis,' § 2 81

[†] It is clear from the form of (44) that, given x and λ, infinitely many values of y satisfy the equation Only the numerically least of these is of importance

$\lambda = 1$ It is convenient to treat the solutions when λ is integral separately There are four, and no more, distinct cases, Types I–IV below

Type I —

$$\left.\begin{aligned} W &= w_1 + w_2 \cos 2\theta + w_3 \cos 4\theta + \dots, \\ \phi &= \phi_1 \sin \theta + \phi_2 \sin 3\theta + \phi_3 \sin 5\theta + \dots, \end{aligned}\right\}$$

giving the equation

$$\begin{vmatrix} F(0) + y, & \frac{3x}{2}, & 0 & 0, & \cdot \\ -x & F(1), & \frac{x}{2} & 0, & \\ 0, & -\frac{3x}{2}, & F(2) + y, & \frac{3x}{2}, & \\ 0, & 0, & -\frac{x}{2}, & F(3), & \end{vmatrix} = 0$$

Type II —

$$\left.\begin{aligned} W &= w_1 \sin \theta + w_2 \sin 3\theta + w_3 \sin 5\theta + \dots, \\ \phi &= \phi_1 + \phi_2 \cos 2\theta + \phi_3 \cos 4\theta + \dots, \end{aligned}\right\}$$

$$\begin{vmatrix} F(0), & -\frac{x}{2}, & 0, & 0, \\ 3x, & F(1) + y, & -\frac{3x}{2}, & 0, \\ 0 & \frac{x}{2}, & F(2), & -\frac{x}{2}, \\ 0, & 0, & \frac{3x}{2}, & F(3) + y, \end{vmatrix} = 0$$

Type III —

$$\begin{aligned} W &= w_1 \cos \theta + w_2 \cos 3\theta + w_3 \cos 5\theta + \dots, \\ \phi &= \phi_1 \sin 2\theta + \phi_2 \sin 4\theta + \phi_3 \sin 6\theta + \dots, \end{aligned}$$

$$\begin{vmatrix} F(1) + y, & \frac{3x}{2}, & 0, & 0, & \cdot\cdot \\ -\frac{x}{2}, & F(2), & \frac{x}{2}, & 0, & \cdot\cdot \\ 0, & -\frac{3x}{2}, & F(3) + y, & \frac{3x}{2}, & \\ 0, & 0, & -\frac{x}{2}, & F(4), & \end{vmatrix} = 0$$

Type IV :—

$$W = w_1 \sin 2\theta + w_2 \sin 4\theta + w_3 \sin 6\theta + \ldots ,$$

$$\phi = \phi_1 \cos \theta + \phi_2 \cos 3\theta + \phi_3 \cos 5\theta + \ldots ,$$

$$\begin{vmatrix} F(1), & -\frac{x}{2}, & 0, & 0, \\ \frac{3x}{2}, & F(2) + y, & -\frac{3x}{2}, & 0, \\ 0, & \frac{x}{2}, & F(3), & -\frac{x}{2}, \\ 0, & 0, & \frac{3x}{2}, & F(4) + y, \end{vmatrix} = 0$$

If the first term of W is taken to be the sine or cosine of any integral multiple of θ, one or other of these four forms is reached. Types I and IV correspond to $\lambda = 0$ in the general solution, Types II and III to $\lambda = 1$. It appears that on putting $\lambda = 0$ the determinant of (44) becomes the product of the determinants corresponding to Types I and IV, and similarly in case $\lambda = 1$, but this has not been verified algebraically.

§ 11. *Numerical Results.*—Theoretically, values of y are required for all values of μ', but the sequel will show that when μ' is large the values of y' are of no importance.

Table I gives the relation obtained by computation between y and μ' for the values 10 and 5 of d'.

Table I.—Relation between y and μ' when $\sigma = 0$

(*a*) $d' = 10$ (*b*) $d' = 5$

μ'	y	$-C_1'\mu'^2$	Type	μ	$-y$	$-C_1'\mu'^2$	Type
0·1	0·0148	0·493	I	0·1	0·00378	0·126	I
0·2	0·222	1·85	I	0·2	0·0570	0·475	I
0·3	0·999	3·70	I	0·3	0·262	0·970	I
0·32	1·25	4·07	I	0·4	0·724	1·51	I
0·3	1·22	4·52	III	0·5	1·50	2·00	I
0·4	1·46	3·04	III	0·6	2·56	2·37	I
0·5	1·82	2·43	III	0·5	1·63	2·17	III
0·6	2·36	2·19	III	0·6	1·98	1·83	III
0·7	3·10	2·11	III	0·7	2·44	1·66	III
0·8	4·09	2·13	III	0·8	3·04	1·58	III
0·9	5·35	2·20	III	0·9	3·80	1·56	III
1·0	6·91	2·30	III	1·0	4·74	1·58	III
1·5	19·5	2·89	III	1·1	5·89	1·62	III

The numerical work for the single case $d' = 10$, $\mu' = 1\cdot5$, which gives the largest value of x, will illustrate the method, and show how many rows and columns of the determinant need be considered. In this case $x = 22\cdot5$.

$$F(1) = 10\cdot563, \qquad F(2) = 39\cdot063,$$
$$F(3) = 126\cdot59, \qquad F(4) = 333\cdot09.$$

If $-y = 19$, the determinant of Type III is

$$\begin{vmatrix} -8\cdot437, & 33\cdot75, & 0, & 0, \\ -11\cdot25, & 39\cdot063, & 11\cdot25, & 0, \\ 0, & -33\cdot75, & 107\cdot59, & 33\cdot75, \\ 0, & 0, & -11\cdot25, & 333\cdot09, \end{vmatrix},$$

while if $-y = 20$, it is

$$\begin{vmatrix} -9\cdot437, & 33\cdot75, & 0, & 0 \\ -11\cdot25 & 39\cdot063, & 11\cdot25, & 0 \\ 0, & -33\cdot75, & 106\cdot59, & 33\cdot75, \\ 0, & 0, & -11\cdot25, & 333\cdot09, \end{vmatrix}.$$

The value of the first is

$$(-8\cdot437)(-5\cdot94)(43\cdot7)(341\cdot8),$$

and that of the second

$$(-9\cdot437)(-1\cdot17)(-218)(331\cdot4). .$$

Considering only three rows and columns we have to take only three factors; by linear interpolation it is found that the determinant vanishes when $-y = 19\cdot5$, to three figures. This result is not altered by including the fourth factors. Consequently in all cases considered at most only four rows and columns are needed, and the position is the same when σ is not zero.

The values of $-y$ in Table I are (with some obvious exceptions) the least that lead to non-zero solutions of equations (41) and (42), the type of solution giving them being shown. The proof that there are no smaller values is mainly numerical, but some general arguments are available.

With the solution of Type IV the determinant is positive unless $-y$ exceeds $F(2)$, that is $(4 + \mu'^2)^2$. This expression is greater in every case than the value of $-y$ given.

The determinant corresponding to Type II can be reduced to

$$\mathrm{F}(0)\begin{vmatrix} \mathrm{F}(1)+\dfrac{3x^2}{2\mathrm{F}(0)}+y & -\dfrac{3x}{2} & 0 \\ \dfrac{x}{2} & \mathrm{F}(2) & \dfrac{x}{2} \\ 0 & \dfrac{3x}{2} & \mathrm{F}(3)+y \end{vmatrix}$$

which is positive unless $-y$ exceeds $3x^2/2\,\mathrm{F}(0)$. This expression is $3d^2/2$ and therefore is 150 when $d = 10$ and 37·5 when $d = 5$. Types II and IV are consequently excluded from consideration in the range of values of μ taken.

With Type III $-y$ must exceed $\mathrm{F}(1)$ and therefore 1 and need not be considered till $\mu > 0·3$ when $d = 10$ nor till $\mu > 0·4$ when $d = 5$.

As stated, there is some reason to suppose that the general solution for values of λ other than 0 or 1 cannot provide a minimum value, but it seemed advisable to verify this numerically in some particular cases. When $d = 10$ this work has been confined to the values 0·3, 0·5, 1·0 and 1·5 of μ. In all four cases it has been shown that with the value of $-y$* given in Table I and with each one of the values 0·2, 0·5 and 0·8 of λ the relevant determinant is positive. It was clear that there was no possibility of a smaller root, and further that in case $\mu = 0·3$ the determinant increased with λ while with the other values of μ the contrary was the case. Similar work has been done for the values 0·4 and 1·0 of μ when $d = 5$. These considerations appear adequate to show that the least values of y have actually been found.

The results are shown in fig. 2. The physical significance of y and $\mathrm{C}_1\mu^2$ is explained later after the more practical results for $\sigma = \frac{1}{4}$ have been obtained.

§ 12. *Results when* $\sigma = \frac{1}{4}$.—If σ is not zero but, as is here supposed, $\frac{1}{4}$, the procedure of the last paragraph is not essentially altered. Assuming a value of $\mathrm{C}_1\mu^2$ those of a, y, z, F and G can be calculated from equations (33) to (40) and the value of $\mathrm{C}_1\mu^2$ for which the appropriate determinant vanishes is found by linear interpolation as before. The type solutions of § 10 may be used without alteration, the determinants corresponding to Types I and III being now

$$\begin{vmatrix} \mathrm{F}(0)+y & \mathrm{F}/2 & 0 & 0 \\ -\mathrm{G} & \mathrm{F}(1) & \mathrm{G}/2 & 0 \\ 0 & -\mathrm{F}/2 & \mathrm{F}(2)+y+4z, & \mathrm{F}/2 \\ 0, & 0 & -\mathrm{G}/2 & \mathrm{F}(3) \end{vmatrix}$$

---

* That corresponding to Type I was of course used for $\mu' = 0·3$.

and

$$\begin{vmatrix} F(1)+y+z, & F/2, & 0, & 0, \\ -G/2, & F(2), & G/2, & 0, \\ 0, & -F/2, & F(3)+y+9z, & F/2, \\ 0, & 0, & -G/2, & F(4), \end{vmatrix},$$

respectively

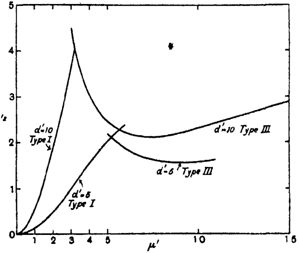

Fig 2.—Values of $C_1'\mu'^2$, when $\sigma = 0$.

The results of calculation are given in the following table

Table II —Relation between $C_1'\mu'^2$ and μ' when $\sigma = \frac{1}{4}$

(a) $d' = 10$			(b) $d' = 5$		
μ'	$-C_1'\mu'^2$	Type	μ'	$-C_1'\mu'^2$	Type
0 1	0 465	I	0 1	0 119	I
0 2	1 77	I	0 2	0 454	I
0 3	3 60	I	0 3	0 945	I
0 325	4 09	I	0 4	1 50	I
0 3	4 45	III	0 5	2 03	I
0 4	2 99	III	0 6	2 44	I
0 5	2 40	III	0 5	2 12	III
0 6	2 15	III	0 6	1 80	III
0 7	2 08	III	0 7	1 64	III
0 8	2 10	III	0 8	1 57	III
0 9	2 16	III	0 9	1 55	III
1 0	2 26	III	1 0	1 57	III
1 2	2 49	III	1·1	1 61	III
1 5	2 84	III	1 2	1 67	III
			1·5	1 93	III

The values of $C_1'\ \mu'^2$ in this table are in all cases within 7 per cent of the corresponding values when $\sigma = 0$ This being so there appeared to be no need to repeat the numerical work of verifying that the favourite types have actually been obtained, especially as the general remarks of § 11 apply with little alteration to this case The results are shown in figs 3 and 4

§ 13 The collapsing thrust* is $-2\ E\,h\,T_1/(1-\sigma^2)$, and the corresponding stress is therefore proportional to T_1 or C_1, while

$$C_1 - C_1'\,h^2\,\mu^2 = (\pi h/l)^2\,(C_1'\ \mu'^2), \tag{45}$$

being the length of a bay

Before proceeding further it must be pointed out that in this, as in most other problems of elastic stability, it is impracticable to consider in detail how the plate is held at its edges For instance, in the investigation of the stability under longitudinal thrust of a cylindrical strut, the condition for the collapse of a strut of length λ under given end conditions has not been found, what has been done is to find what thrust will maintain a distortion of wave length λ in an indefinitely long tube †

From (31) $\lambda\ (=\pi/\mu)$ is the distance between successive zeros of w', the normal displacement in the distortion, and the best way to bring H, the height of the

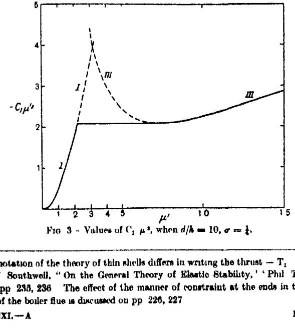

FIG 3 - Values of $C_1\ \mu'^2$, when $d/h = 10$, $\sigma = \frac{1}{4}$.

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[*] The notation of the theory of thin shells differs in writing the thrust $-T_1$

[†] R. V Southwell, "On the General Theory of Elastic Stability,' 'Phil Trans,' A, vol 213, pp 235, 236 The effect of the manner of constraint at the ends in the similar problem of the boiler flue is discussed on pp 226, 227

plate, into the analysis would appear to be to decide that λ must not exceed H Then μ' ($= \mu/n$) must not be less than l/H The appropriate value of $C_1'\mu'^2$ to be substituted in (45) is the *least* value the expression can take for $\mu' \geqq l/\mathrm{H}$, this is merely to say that the wave length of distortion will be that possible under

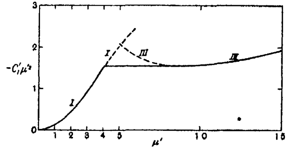

FIG 4 —Values of $C_1\mu'^2$, when $d/h = 5$, $\sigma = \frac{1}{4}$

the least stress Consequently when $d' = 10$, for values of l/H between 0·22 and 0 7 the wave-length is to be calculated from $\mu' = 0\ 7$, and the value of $-C_1'\mu'^2$ is 2 08 This least value can be read off from the continuous line

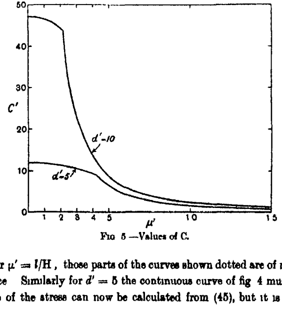

FIG 5 —Values of C.

in fig 3 for $\mu' = l/\mathrm{H}$, those parts of the curves shown dotted are of no physical significance Similarly for $d' = 5$ the continuous curve of fig 4 must be used The value of the stress can now be calculated from (45), but it is simpler to find the relation between a new function C′ and μ', $-C'\mu^2$ being represented by the continuous lines in the two cases This relation is given in the following table and shown in fig 5

Table III Relation between C′ and μ

(a) d 10		(b) d' – 5	
μ	C	μ	C
0 1	46 5	0 1	11 9
0 2	44 2	0 2	11 3
0 225	41 1	0 3	10 5
0 3	23 1	0 4	9 37
0 4	13 0	0 425	8 58
0 5	8 32	0 5	6 20
0 6	5 78	0 6	4 31
0 7	4 25	0 7	3 16
0 8	3 28	0 8	2 42
0 9	2 67	0 9	1 91
1 0	2 26	1 0	1 57
1 2	1 73	1 1	1 33
1 5	1 26	1 2	1 16
		1 5	0 853

The collapsing stress (a thrust) is now

$$\frac{E\pi^2}{1-\sigma^2}\left(\frac{h}{H}\right)^2 C', \tag{4b}$$

the value of C′ being determined for $\mu' = l/H$

§ 14 —The critical stress of a long plane plate of height H and semi thickness h is*

$$\frac{E\pi^2}{3(1-\sigma^2)}\left(\frac{h}{H}\right)^2,$$

so that the ratio of the critical stress of a corrugated plate to that of a plane plate of the same thickness and height is 3C′ From fig 5 if the depth of the bay of a corrugated plate is $10h$ it will withstand over 130 times the stress that can be put on a plane plate of the same thickness and of the same height provided that the ratio of length of bay to height does not greatly exceed 1/5 but with the increase of l/H beyond this point, the strength of the plate diminishes rapidly In the other case $d' = 5$, it is not so important that l/H should be small, a critical stress 30 times that of a similar plane plate can be obtained if l/H is less than 0 35 Even such shallow plates as are considered here are therefore remarkably strong; in the first case, the critical stress (though not, of course, the total thrust per unit length of edge line) is actually greater than that in a plane plate of the same over-all thickness, $2 2h$.

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* Love *op cit* § 332 A

A rough expression for the maximum value of C′ is $d'^2/2$. There is some theoretical basis for this; when $\sigma = 0$ it can be seen from the condition for a solution of Type I that as μ' decreases, $-y$ approaches the value $(1 + 3d'^2/2)\mu'^4$, whence $-C_1' = 1/3 + d'^2/2$. By means of this approximate rule and fig. 5, the values of C′ for all values of d' less than 10 and all μ' can be obtained probably to within 5 per cent.

The limiting value of C′ as μ' is increased is seen immediately; by increasing the length of bay and keeping the height constant the case of the plane plate is approached. Hence C′ tends to the value 1/3. The distortion of a plane plate corresponds to the solution of Type I in the corrugated plate. Consequently it may be expected that for large values of μ' the curves of Type I in figs. 3 and 4 will again intersect those of Type III, and will then remain below them. This is borne out to some extent by the point of inflection on the Type I curve when $d' = 5$; when $d' = 10$ the point of inflection is on a part of the curve not drawn.

§ 15. The method of reduction of § 6 is not available if the assumption that the depth of bay is comparable with the semi-thickness is abandoned. An extension of the theory to plates with deeper bays, though certainly possible if it is supposed that $\sigma = 0$, must therefore entail considerable labour, and it is only by this extension that it is possible to estimate within what limits d' must lie if the approximations of the preceding work are to be valid. It does not appear worth while to attempt this until it is known from experiment what features of the problem are missed by the approximations. Again the rough rule that the ratio of the critical stress in a corrugated plate to that in a similar plane plate is, in the most favourable conditions, $3d'^2/2$, indicates that by increasing d' a point is rapidly reached, even with the thinnest plates, beyond which Hooke's law will no longer hold, and the possibility of elastic failure (as opposed to failure by instability) must be taken into account. Suppose that $E = 2{\cdot}0 \times 10^{12}$ (C.G.S.), and that the limit of proportionality is $4{\cdot}6 \times 10^9$,* then if $h/H = 0{\cdot}01$, the critical stress given by the rough approximation exceeds the limit of proportionality as soon as $d' = 2{\cdot}1$; if $h/H = 0{\cdot}005$, the corresponding value of d' is twice that above, $4{\cdot}2$. Now the smaller is h/H, the greater is the range of values of d' in which the work of this paper will be valid, so that there is some hope that with values of h/H likely to occur in practice the solution will hold in all cases in which break down is due to instability alone, or at any rate in all cases wherein the critical stress can be calculated by a theory based on Hooke's law. When elastic failure must be considered, theory can at present do no more than indicate a stress that cannot in any circumstances be exceeded; theoretical values in such of these cases as have been worked out are usually far in excess of the stresses that actually cause failure.* The rapidly increasing maximum stress given by the ratio $3d'^2/2$ is not likely to hold for large values of d' (it is 4 per cent too high when $d' = 5$, and 6 per cent too high when $d' = 10$), and there is some reason therefore to conclude that this stress is one that cannot be exceeded in any case. If this is so, where extension of this work is needed is in finding whether the theory can set a lower limit to the maximum stress for larger values of d'.

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* The writer is indebted to Mr. H. J. Gough of the National Physical Laboratory for these figures, which are average values for some types of steel used in aeroplane construction.

It may be pointed out again that it has not been found possible to allow for the way in which the plate is held at its edges; there is, however, no evidence that on this account the theoretical values of the stress are likely to be too low. It is true that by clamping a plane plate the critical stress is increased to four times that given by the above formula, because the wave-length of distortion is halved. But the effect of clamping, or any method of support, in any other case is that high local stresses, and therefore conditions likely to lead to instability, result in the neighbourhood of the edges, due to what is usually known as the "edge effect."† It is true that if $\sigma = 0$ the way in which the plate is held at the edges can be considered; but it is only in a certain type of problem that the value of σ is of minor importance, and those that concern the edge effect, which does not take place at all if $\sigma = 0$, are certainly not in this class.

§ 16. The utility of a theoretical discussion of the stability of a body is not, however, confined to the deduction of a formula for the critical stress; there is indeed, for the reason mentioned, but rarely agreement with experiment on this point. Qualitative information, with usually a wider range of validity, can often be obtained. Thus it may be concluded by extrapolation from fig. 5 that for values of d' up to 15 or 20, any value of l/H not exceeding 1/5 will lead to roughly the maximum stress possible in a plate of given depth of bay, and this is a result likely to be true when the theoretical value of the critical stress is unreliable.

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* Southwell, *loc. cit.*, footnote to p. 241.

† Love, *op. cit.*, § 339 (*b*).

Again, theoretical information in respect of the favourite type of distortion is usually in good agreement with practice This matter has not been considered here in detail, as there is little point in elaborating the above work before experimental results are available, but the general nature of the distortion can be stated The highest stress is obtained when the ratio of length of bay to height is small, and then the distortion of Type I takes place This resembles that of a long plane plate, or, what is perhaps a closer analogy, the primary flexure of a cylindrical strut under thrust, in which the strut as a whole bends like a thin solid rod The normal displacement w' of a point of the plate is of the form

$$w' = (w_1 + w_2 \cos 2n\beta + \quad) \sin \frac{\pi\alpha}{H},$$

where w_1, w_2, are constants whose ratios can be determined, for when the ratio of length of bay to height is small, the wave-length of distortion is as long as possible, moreover, in this case, the most important term in the bracket is w_1, so that the normal displacement is practically dependent only on α * The tangential movement of points of the plate is of minor importance

The distortion of Type III is not of the same practical importance, for it only appears when the plate is not so corrugated as to give nearly the maximum stress for given depth of bay and height In this,

$$w' = (w_1 \cos n\beta + w_2 \cos 3n\beta + \quad) \sin \mu\alpha,$$

where μ is not now necessarily equal to π/H, and exceeds this value over a certain range of values of l/H, so that a distortion of short wave-length takes place Again there is a parallel to this in the stability of a cylindrical strut The distortion cannot be simply described in this case as certainly two terms of the series are needed, and they are likely to be of equal importance, but it is of interest to notice that the middle generator (*i e*, $n\beta = (2m + 1)\pi/2$, m integral), of any bay remains fixed in the displacement

§ 17 *Notation*—It may be useful to set down again here the notation for convenience in reading the figures

$d' = d/h$, where d is the depth of a bay, and h the semi-thickness of the plate

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* The number of terms that must be taken in the series for the displacements is indicated by the number of rows of columns of the determinant necessary to ensure a given accuracy. In the work above four rows and columns are in all cases found sufficient, so that two terms of the series for w' give a result of the same accuracy, but when l/H is small, two rows and columns are generally enough, and w' is therefore roughly a function of α only

$n = \pi/l$, $\mu = \pi/\lambda$ and $\mu' = \mu/n$, l is the length of a bay of the plate, and λ the distance between consecutive zeros of w', the normal displacement in the distortion. λ, the semi-wave length of distortion, will be that possible under the least stress, but we may suppose that λ must not exceed H, the height of the plate. The proper value of μ' is then the value $\geqq l/H$ that gives the least stress; the fact that μ' is not in every case equal to l/H is allowed for by the continuous straight lines in figs. 3 and 4.

The critical stress is

$$-\frac{E\pi^2}{1-\sigma^2}\left(\frac{h}{l}\right)^2 C_1'\mu'^2,$$

the appropriate value of $C_1'\mu'^2$ is that given by the continuous lines in figs. 3 and 4 for the value l/H of μ'.

Fig. 5 gives the relation between a new variable C′ and μ'. The critical stress is

$$\frac{E\pi^2}{1-\sigma^2}\left(\frac{h}{H}\right)^2 C',$$

the value of C′ being taken from fig. 5 for the value l/H of μ'. 3C′ is, therefore, the ratio of the critical stress in the corrugated plate to that in a plane plate of the same thickness and height.

Quartet Terms in the Arc Spectrum of Copper.

By C. S. Beals, M.A., D.I.C.

(Communicated by Prof. A. Fowler, F.R.S.—Received January 8, 1926.)

[Plate 3.]

Introductory.

The arc spectrum of copper in common with the spectra of other elements in the first group of the Periodic Table has been shown to contain a system of doublet series. The chief lines of copper were classified by Rydberg[*] and by Kayser and Runge.[†] Some additional combinations were discovered by Dunz[‡] and the series have since been re-tabulated by Fowler.[§]

Only one member of the principal series of copper has been identified with certainty, though Fowler gives five members of the diffuse and six members of the sharp series. An interesting feature of the series system of copper is the occurrence of a somewhat abnormal term, designated as X, which combines with the two members of the doublet *p* level, forming the well known doublet λ 5700 25, λ 5782 16. The nature of the combination with the doublet *p* terms, and the Zeeman effect,[||] showed the X-term to be a doublet *d* term with inner quantum number 2. It was to be expected that this term would have a companion term with inner quantum number 3, but the earlier investigators failed to find this term. The identity of the missing term has been made clear in a recent paper by Shenstone[¶] who gives the numerical value of the term as 51105 5, the value of 51105 0 having previously been suggested by Ruark and by Werner. The numerical value of the term X is given by Fowler as 49062 6. It follows that the difference $d_3 - d_2$[**] = 2042 9 and the complete $d - p$ doublet includes the line λ 5105 55.

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[*] Rydberg, 'La Constitution des spectres d'Emission," 'Memoir présenté à l'Académie Royal des Sciences, November, 1889.

[†] Kayser and Runge, "Über die spectren der Elemente," 'Abh. d. Berlin Akademie,' 1892.

[‡] Dunz, 'Bearbeitung unserer Kentnisse von den Serien," 'Dissert. Tübingen,' 1911.

[§] Fowler, 'Report on Series in Line Spectra,' Fleetway Press, London, 1922.

[||] Paschen Goetz, 'Seriengesetze der Linien spectren.'

[¶] Shenstone, 'Bull. Amer. Phys. Soc.,' vol. 1, No. 1, p. 6 (1925), and 'Phil. Mag.,' vol. 49 (May, 1925).

[**] In the notation of Russel and Saunders these irregular doublet terms would be designated as d'', but as they are the only terms of this type which are dealt with in the present paper, they will be sufficiently distinguished by the omission of the total quantum number *m*.

In the same paper Shenstone gives the results of an extended investigation of the copper spectrum Values are given for a considerable number of new terms, many of which have been shown to combine with the two high *d* terms which have just been discussed Many of the terms have not been definitely identified and the suggestion is made that the spectrum of copper may be found to contain quartets The results of further work by the same author have appeared in a recent letter to "Nature"* A number of additional terms are given, some of which have negative values Azimuthal and inner quantum numbers have been provisionally assigned to the terms on the basis of their combinations with the doublet terms d_2 and d_3 As Shenstone states, quartet terms are undoubtedly involved though no complete multiplet structures were then indicated

Previous to the publication of Shenstone's work, the present writer had undertaken a series of observations of the magnetic resolutions shown by copper arc lines, and it was hoped that the results of this investigation would make it possible to classify some of those lines which had not already been resolved into series The fact of the existence of a considerable number of constant difference relations, having no obvious relation to the doublet series in the arc spectrum of copper, was first pointed out by Rydberg † The work of Shenstone has made these relations considerably more intelligible though Zeeman measurements have been found to be necessary in order definitely to identify the terms The complex nature of the copper spectrum had made it probable that higher multiplicity terms were involved and the results of the present investigation have shown beyond doubt that this is the case A number of complete quartet multiplets have been identified and many of the terms discovered by Shenstone have been shown to be quartet terms

The present paper gives particulars of the new regularities which have been discovered The greater number of the terms which have been included in the present analysis have already been given in one or other of Shenstone's papers, though many of them were independently discovered by the author before access was had to Shenstone's work As Shenstone has already shown, a number of the newly-discovered terms combine with terms of the old doublet system, and this fact has made it possible to calculate the absolute values of the new terms

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* Shenstone, 'Nature,' vol 116, p 467 (September 26 1925)

† Rydberg, 'Astrophys Jour,' vol 6, p 239 (1897)

Observational Data

For the purposes of the present investigation, photographs have been taken of the copper spectrum over a range which extended from λ 2000 to λ 6700. Some of the photographs were taken with a large Hilger quartz spectrograph, but most of the work has been done with a ten-feet concave grating in an Eagle mounting. This instrument has been used for the observation of the ordinary arc spectrum and also to determine the behaviour of the copper lines in a magnetic field. The apparatus necessary to observe the arc in the magnetic field has been described in a previous paper by the author on the spectrum of palladium.* In the present work, only the arc in air has been used as a source of light, and with the exception of certain lines in the visible region, most of the classified lines have been found to be of sufficient sharpness for reasonably good determination of Zeeman effects. In order to secure the necessary resolution, some use has been made of all the orders of the grating up to the fifth. Of the photographs of Zeeman effects which are reproduced on Plate 3, the lines of wave-length longer than λ 4000 represent second or third order spectra, while the photographs of the shorter wave-length lines were taken in the fourth and fifth orders of the grating. The observations of Zeeman effects have not been extended below λ 2300.

The wave-lengths and wave-numbers of the lines which are included in the present analysis have been collected in Table I. One line, λ 4069.44, does not appear to have been previously recorded and has been measured by the present writer. The behaviour of copper lines in the magnetic field has been indicated in Table I by placing opposite to each line the measurements of the Zeeman components which have been observed. In accordance with the usual practice, the figures represent fractions of the normal Zeeman resolution as shown by the separation of components in lines of a singlet system. The value of the normal resolution has been calculated from measurements of the patterns shown by the calcium doublet λ 3968.46, λ 3933.66, resolutions (0.66) 1.33 and (0.33) 1.00, 1.66, and the zinc line λ 4680.20 which exhibits the resolution (0.00) 2.00. For purposes of comparison, the calculated Zeeman resolutions have been placed beside the observed effects. The term combinations have also been indicated, in the final column of Table I.

The value of the theoretical Zeeman resolutions have either been taken directly from the book 'Zeemaneffekt und Multipletstruktur,' or have been calculated, using the rules of Back and Landé.†

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* Beals, 'Roy. Soc. Proc.,' A, vol. 109, p. 369 (October, 1925).

† Back and Landé, 'Zeemaneffekt und Multipletstruktur,' Berlin (1925).

Table I.

λ (Int.)	ν	Zeeman Effect (Observed)	Zeeman Effect (Calculated)	Combination
5554 94 (3)	17997 1	(0 00) 1 88	(0 03, 0 09, 0 14) 1 29, 1 34, 1 40, 1 46, 1 51, 1 57	$a^4d_3 - {}^4d_4$
5432 05 (1u)	18404 2	—	—	$a^4d_2 - {}^4d_3$
5391 67 (2u)	18542 0	—	—	$a^4d'_3 - {}^4d_3$
5360 04 (1)	18651 4	Broadened	—	$y_1 - {}^4d_1$
5355 00 (1u)	18668 9	—	—	$a^4d_1 - {}^4d_2$
5352 68 (2)	18677 0	(0 00) 2 14	—	$x_3 - {}^4d_4$
5292 54 (5)	18889 3	(0 00) 1 44	(0 00) 1 43	$a^4d_4 - {}^4d_4$
5250 60 (1u)	19040 1	—	—	$a^4d'_3 - {}^4d_2$
5212 89 (1u)	19177 9	—	—	$a^4d'_2 - {}^4d_3$
5200 87 (2u)	19222 2	—	—	$r_3 - {}^4d_3$
5144 12 (1u)	19434 3	—	—	$a^4d'_4 - {}^4d_3$
5111 94 (2)	19558 6	(0 00) 0 00	(0 00) 0 00	$a^4d_1 - {}^4d_1$
5034 32 (1u)	19858 1	—	—	$r_2 - {}^4d_2$
5016 63 (3)	19928 2	(0 55) 0 55, 1 63	(0 60) 0 60, 1 80	$a^4d_2 \quad {}^4d_1$
4842 20 (1u)	20646 1	—	—	${}^4f_2 - {}^4d_3$
4797 04 (2)	20840 4	(0 00) 2 20	(0 20, 0 60, 1 00) 0 43, 0 83, 1 23 1 63, 2 03, 2 43	${}^4f_3 - {}^4d_4$
4704 60 (6)	21249 9	(0 64) 1 40	(0 09, 0 28, 0 47, 0 66) 0 76, 0 95 1 14, 1 33, 1 52 1 61, 1 70	${}^4f_4 - {}^4d_4$
4697 49 (4u)	21282 0	—	—	${}^4f_3 - {}^4d_3$
4674 76 (6u)	21385 4	—	—	${}^4f_2 - {}^4d_2$
4651 13 (8)	21494 1	(0 00) 1 20	(0 05, 0 14, 0 24, 0 33) 1 00, 1 10 1 19 1 29, 1 38, 1 48, 1 57, 1 67	${}^4f_5 - {}^4d_4$
4586 97 (7u)	21794 8	—	—	${}^4f_4 - {}^4d_3$
4539 70 (5u)	22021 7	—	—	${}^4f_3 - {}^4d_2$
4509 40 (4)	22169 7	(0 23) 0 23, 0 64	(0 20) 0 20, 0 60	${}^4f_2 \quad {}^4d_1$
4415 60 (3u)	22640 7	—	—	${}^4p_1 - {}^4d_2$
4378 20 (6u)	22834 1	—	—	${}^4p_2 - {}^4d_3$
4275 13 (8)	23384 6	(0 00) 1 18	(0 09, 0 26, 0 43) 1 00, 1 17, 1 34, 1 51 1 68, 1 85	${}^4p_3 \quad {}^4d_4$
4259 43 (3u)	23470 8	—	—	${}^4p_2 - {}^4d_2$
4248 97 (4)	23528 6	(1 30) 1 30	(1 33) 1 33	${}^4p_1 - {}^4d_1$
4177 76 (4u)	23929 7	—	—	${}^4p_3 - {}^4d_3$
4104 23 (2)	24358 3	(0 87) 0 87, 2 62	(0 81) 0 81, 2 60	${}^4p_2 - {}^4d_1$
4069 44 (0u)	24566 6	—	—	${}^4p_3 - {}^4d_2$
3720 77 (2)	26868 1	—	—	${}^2d_2 \quad {}^4p_2$
3609 30 (2)	27698 3	(0 91) 0 00	(0 93) 0 01, 1 73	${}^2d_2 - {}^4p_1$
3594 02 (2)	27816 1	0 99	(0 20, 0 60, 1 00) 0 60, 1 00, 1 40, 1 80, 2 20	${}^2d_3 - {}^4p_3$
3530 99 (6)	28317 4	(0 00) 1 20	(0 01, 0 34) 0 68, 0 91, 1 14, 1 37	${}^2d_3 - {}^4f_3$
3457 86 (3)	28911 3	(0 25, 0 79) 0 33, 0 84	(0 27, 0 80) 0 40, 0 93, 1 47, 2 00	${}^2d_2 - {}^4p_2$
3440 52 (3)	29057 1	0 60	(0 20, 0 60) 0 20, 0 60, 1 00	${}^2d_2 - {}^4f_2$
3337 85 (6)	29950 7	(0 00) 1 26	(0 02, 0 06, 0 10) 1 14, 1 18, 1 22, 1 26, 1 30, 1 34	${}^2d_3 - {}^4f_4$
3279 82 (3)	30480 7	(0 00) 1 56	—	${}^2d_3 - x_3$
3208 23 (4)	31160 3	(0 19, 0 57) 1 67	(0 28, 0 85) 0 51, 1 08, 1 66, 2 23	${}^2d_3 - a^4d'_3$
3194 10 (6)	31298 7	(0 39) 1 18	(0 20, 0 60) 0 60, 1 00, 1 40	${}^2d_2 - a^4d'_2$
3156 63 (5)	31670 3	(0 31) 1 10	(0 40) 0 40, 1 20	${}^2d_2 - a^4d'_1$
3093 99 (6)	32311 3	(0 00) 1 78	(0 11, 0 34, 0 57) 0 85, 1 08, 1 31, 1 54, 1 77 2 00	${}^2d_3 - a^4d'_4$
3073 80 (4)	32523 6	(0 30) 1 10	—	${}^2d_2 - x_3$
3068 91 (2)	32575 4	—	—	${}^2d_2 - y_1$
3063 42 (6)	32633 8	(0 60) 1 13	(0 20, 0 60) 0 60, 1 00, 1 40	${}^2d_2 - b^4d'_2$
3036·10 (6)	32927 4	(0 42) —	(0 20, 0 60) 0 60, 1 00, 1 40	${}^2d_2 - c^4d'_2$
3024 99 (2)	33048 4	—	—	$1^2p_1 - {}^4d_2$
3010 84 (6)	33203 6	(0 00) 1 19	(0 08, 0 25, 0 43) 0 94, 1 11, 1 28, 1 45, 1 62	${}^2d_3 - a^4d'_3$
2998 38 (2)	33341 6	—	—	${}^2d_2 - a^4d'_3$
2997·36 (4)	33352 8	(0 21, 0 68) 1 85	(0 28, 0 85) 0 51, 1 08, 1 66, 2 23	${}^2d_3 - c^4d'_3$
2961·18 (6)	33760 4	(0 00) 1 22	—	$d_3 - \mathrm{G}$
2882 94 (4)	34676 7	(0 00) 1 22	(0 00) 1 20	${}^2d_3 - b^4d'_3$
2858·74 (2)	34970 1	—	—	${}^2d_2 - c^4d'_2$
2824 37 (6)	35395 7	(0 00) 1 24	(0 08, 0 25, 0 43) 0 94, 1 11, 1 28, 1 45, 1 62	${}^2d_3 - c^4d'_3$

Table I continued

λ (Int)	ν	Zeeman Effect (Observed)	Zeeman Effect (Calculated)	Combination
2768 89 (9)	36105 1		—	${}^2d_3 - c^4d_4$
2766 39 (8)	36137 6		—	${}^2d_3$ A
2618 38 (10)	38180 3		—	${}^2d_3 - A$
2492 14 (7R)	40114 1	(0 30) 1 0	(0 13) 0 93 1 00	$1^2s_1 - {}^4p_2$
2441 62 (4R)	40944 0	(0 00) 2	(0 33) 2 33	$1^2s_1 - {}^4p_1$
2406 66 (5)	41538		—	${}^2d_3 - B$
2369 87 (6)	42181 8	0 00) 1 33	(0 03 0 08) 0 77 0 83 0 88 0 94	${}^2d_2 - {}^4f_3$
2319 56 (3)	43098 4		—	${}^2d_2 - C$
2303 11 (4)	43406 2			${}^2d_2 - D$
2293 83 (8R)	43581 7			${}^2d_3 - B$
2260 49 (4)	44221 5			${}^2d_3 - {}^4f_4$
2244 24 (2)	44544 6			$1^2s_1 - {}^4d_2$
2225 66 (2)	44916 5			$1^2s_1 - {}^4d_1$
2214 56 (6R)	45141 5		—	${}^2d_3 - G$
2199 65 (6R)	45447 6			${}^2d_3 - D$
2181 68 (1)	45821			$1^2s_1 - y_1$
2178 91 (1r)	45880 0			$1s_1$ b^4d_2
2171 75 (3)	46031 4			${}^2d_2 - E$
2165 06 (1n)	461 3 6			1^2s_1 a^4d_2
2112 02 (2)	47348 0			${}^2d_2 - F$
2079 47 (4n)	48073 7		—	${}^2d_3$ F
2024 05 (5R)	49389 8		—	${}^2d_3 - E$

Notation.

For use in the tables and the discussion which follows a uniform system of notation has been adopted in accordance with a suggestion made to the author by Prof Fowler Different values of the azimuthal quantum number k are indicated by the small letters s p d, f corresponding to the values $k =$ 1 2 3 4 The maximum multiplicity of the system (doublet quartet etc) is indicated by placing a small index to the left and slightly above the letter representing the azimuthal quantum number of the term The inner quantum numbers in accordance with recent practice are indicated as subscripts Thus the symbol ${}^4p_2$ represents a quartet p term with inner quantum number 2 The combinations which have been found to take place include doublets quartets and inter combination lines The combinations thus follow the rule $\Delta r = 0$ or ± 1 where r denotes the maximum multiplicity in the system For the transitions of the azimuthal quantum numbers the ordinary terms follow the rule $\Delta k = \pm 1$ The primed terms in general follow the rule $\Delta k = 0$ though in some cases the transition $\Delta k = 2$ takes place The inner quantum numbers of both types of terms follow the uniform rule $\Delta j = 0$ or ± 1

The Quartet Combinations

The three groups of lines whose wave numbers are given in Table II are formed by combinations between terms of a quartet system The identification of terms has been made through a consideration of the Zeeman effects in connection with the constant difference relations and the inner quantum selection rules As has already been mentioned the observed and calculated Zeeman effects for the lines are contained in Table I A reference to this table will show the agreement which has been obtained between observation and theory In some cases it has not been possible to obtain complete resolution, but there is a sufficient number of clearly resolved patterns to make the present assignment of terms reasonably certain It will be observed that the combinations formed represent transitions from a quarter *d* level characterised by negative terms, to a number of other lower levels in which the values assigned to the terms are positive An examination of the numerical values which are given to the terms will show that all the terms are inverted, that is, the largest term of each level has the largest inner quantum number For the *d* and *f* levels the separation ratios are also inverted, and the smallest separations occur between terms having the largest inner quantum numbers The numerical

Table II Quartet Multiplets

	$^4d_1$	$^4d_2$	$^4d_3$	$^4d_4$
	−2164 3 (88[illegible] 8)	−1276 5 (636 3)	040 2 (545 0)	95 2
$^4p_3$ 23289 4		24566 6 (0u)	23929 7 (4u)	23384 6 (6)
(1095 3)				
$^4p_2$ 22194 1	24358 3 (2)	23470 8 (2u)	22834 1 (6u)	
(829 8)				
$^4p_1$ 21364 3	23528 6 (4)	22640 7 (4u)		
$^4f_5$ 21399 0				21494 1 (8)
(244 2)				
$^4f_4$ 21154 8			21794 8 (7u)	21249 9 (6)
(409 6)				
$^4f_3$ 20745 2		22021 3 (5u)	21385 4 (4u)	20840 4 (2)
(739 7				
$^4f_2$ 20005 [illegible]	22169 [illegible] (4)	21282 0 (4u)	20646 1 (1u)	
a^4d_4 18794 2			19434 3 (1u)	18889 3 (5)
(892 4)				
a^4d_3 17901 8		19177 9 (1u)	18542 0 (2u)	17997 1 (2)
(137 9)				
a^4d_2 17763 9	19028 2 (1	19040 1 (1u)	18404 2 (1u)	
(371 7)				
a^4d_1 17392 2	19556 6 (2)	18068 9 (1u)		
x_3 18581 9		19858 1 1u)	19222 2 (2u)	18677 0 (2)

values of the terms have been derived from intercombination lines and will be discussed in a later section

The grouping of the lines in the pd and fd multiplets is considered to be completely satisfactory both as regards the regularity of the separation ratios and the relative intensities of the lines The Zeeman effects also, in so far as they have been observed, are in remarkably good agreement with the calculated resolutions Photographs have been reproduced of the resolution patterns shown by the combinations $p_2 d_1$, $p_1 d_1$ and $f_2 d_1$

The evidence supporting the present arrangement of the $a\,d'$ terms can scarcely be considered as satisfactory as that which has been found for the f and p levels The terms $a\,d'$ and $a\,d'_2$ appear to be established beyond doubt by the Zeeman effects, shown by the lines λ 5016 63 and λ 5111 94

The resolution shown by the line λ 5292·54 is also satisfactory and confirms the term $a\,d'_4$ For the term $a\,d'_3$, however, the observed Zeeman phenomena are far from being in complete agreement with theory, and the irregularity of the separation ratios makes it somewhat doubtful whether these terms should be grouped together A consideration of the available data has indicated to the author that the arrangement presented in Table II is probably correct, though some ambiguity remains as to the terms $a\,d'_3$ and $a\,d'_4$

The term x_3 has not so far been definitely identified The combinations with the negative quartet terms indicate that it should have the inner quantum number 3, and the term d'_3 is suggested by the intensity relations The evidence given by the Zeeman effects, however, does not support this view, nor do other quartet terms having $j = 3$ satisfy the case It seems possible that there is a new type of regularity involved, and that the x_3 term may be a quartet term which behaves anomalously in the magnetic field Unfortunately the resolution obtained is not sufficiently high to enable definite conclusions to be drawn as to this point

A peculiar feature of the quartet multiplets listed in Table II is the diffuse character of the lines arising from combinations with the terms d_2 and d_3 Ordinarily, evidence of a similarity in general character between the lines of a group is considered to be necessary in order to justify placing them together as a multiplet The fact that lines of different character appear in the multiplets of Table II would at first appear to suggest that grouping the lines together is incorrect Fortunately the Zeeman effects given by the combinations involving the terms d_1 and d_4 serve definitely to identify the terms as quartets, and the present arrangement of the multiplets follows as a necessary consequence of the numerical relations and the relative intensities of the lines

Intercombination Lines

Mention has already been made of the inverted doublet terms $d_2 = 49062\,6$ and $d_3 = 51105\,5$ It has been found that a number of lines in the ultra-violet region of the copper spectrum may be accounted for as combinations between these doublet d terms and the larger quartet terms which have been discussed in the preceding section The wave numbers of these inter-combination lines have been included in Table III Three of the expected combinations are missing but they correspond to less probable transitions of inner quantum numbers The missing combinations are indicated by placing the calculated wave-numbers in brackets The value of the terms ${}^2d_2$ and ${}^2d_3$ are known from their relations with the doublet series system, and this fact has made it possible to calculate the values of the quartet terms The terms given in Tables II and III have been derived in this way A surprising feature of the quartet system is the fact that negative values have to be given to the ${}^4d$ terms

Combinations also take place between a number of the quartet terms and the doublet $1s$ level, which is believed to represent the normal state of the copper atom These combinations have also been indicated in Table III The combination $1^2s - a^4d'$ corresponds to the azimuthal quantum transition $k = 2$ This is one of the less probable combinations and the lines are of comparatively small intensity The lines due to the more probable transition $1^2s - {}^4p$ are much stronger All of the lines formed by combinations with the $1s$ level have been observed by McLennan and McLay* as absorption lines in the spectrum of the neutral vapour of copper

By means of the Zeeman effects which have been observed for the inter-combination lines it is possible to make a further test of the correctness of the azimuthal quantum numbers which have been assigned to the larger quartet terms The resolutions given by combination with the ${}^4f$ and ${}^4p$ terms show particularly good agreement with the calculated patterns. For the a^4d' terms, the measurements show considerable variations from the predicted separations, but the qualitative appearance of the patterns, in so far as they are resolved, is in agreement in every case The Zeeman effects of the combinations due to the transition $1^2s - {}^4p$ are in excellent accord with theory, though the true nature of one of the patterns is somewhat obscured by the fact that the line λ 2492 14 is strongly reversed

Concerning the variations from the predicted separations which have been observed in the Zeeman effects of the inter-combination lines and of the

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* McLennan and McLay, 'Roy Soc Proc,' A, vol. 108, p 515 (1925)

Table III Intercombination Lines

	${}^2d_2$ 49062 6 (2042 9)	${}^2d_3$ 51105 5	1^2s_1 62308 0
${}^4p_3$ 23289 4	[25773 2]	27816 1 (2)	
(1095 3)			
${}^4p_2$ 22194 1	26868 6 (2)	28911 3 (3)	40114 1 (7R)
(829 8)			
${}^4p_1$ 21364 3	27698 3 (2)		40944 0 (4R)
${}^4f_5$ 21399 0			
(244 2)			
${}^4f_4$ 21154 8		29950 7 (6)	
(409 6)			
${}^4f_3$ 20745 2	28317 4 (6)	[30360 3]	
(739 7)			
${}^4f_2$ 20005 5	29057 1 (3)	[31100 0]	
a^4d_4 18794 2		32311 3 (5)	
(892 4)			
$a\ d_3$ 17901 8	31164 8 (4)	33203 6 (8)	
(137 9)			
a^4d_2 17763 9	31298 7 (6)	33341 6 (1)	44544 6 (2)
(371 7)			
a^4d_1 17392 2	31670 3 (2)		44916 5 (2)
x_3 18581 9	30480 7 (3)	32523 6 (4)	

d d quartets it is of interest to note that Back* has recently shown that anomalies of a similar nature occur among the newly-discovered combinations in the spectrum of calcium

A number of lines in addition to those given in Table III show the separation 2042 9 indicating combinations with the inverted ${}^2d$ terms In some cases combinations appear with the doublet $1s$ term as well The Zeeman effects observed for these lines have suggested that some of the terms which may be derived are quartets although they do not combine with the negative quartet terms of Table II The following arrangement is suggested

		${}^2d_2$ 49062 6 (2042 9)		${}^2d_3$ 51105 5		1^2s_1 62308 0	
b^4d_2	16428 8	32633 8	(6)	34676 7	(4)	45880 0	(1*u*)
c^4d_2	16135 2	32927 4	(6)	34970 1	(2)	46173 6	(1*u*)
c^4d_3	15709 8	33352 8	(4)	35395 7	(6)		
c^4d_4	15000 4			36105 1	(3)		

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* Back Zeit f Phys No 77 vol 8 p 579 (1925)

As the Zeeman effects are not all fully resolved some uncertainty remains as to the correctness of the above assignment of terms Shenstone has observed these combinations and has suggested that the terms 16428 8 and 16135 2 are *p* terms

An isolated line has been observed which may correspond to the combination $1^2p_1 - {}^4d_2$ The wave number of the line and the terms are shown below—

	$^2p_1$ 31772 8
$^4d_2$ — 1276 5	33048 4 (2)

As the more probable combinations $^2p_2 - {}^4d_2$ does not occur it is possible that the relation is accidental

A feature of some interest which has been noted in the present research is the behaviour of the line λ 5360 04 in the magnetic field This line was at first thought to be unaffected by the field but when observed with higher resolving power was seen to be slightly broadened The amount of the separation appears to be too small to identify with any of the calculated doublet or quartet patterns The sharpness of the line and the region in which it falls has suggested a combination with the term $^4d_1$ The new term which has been derived in this way is designated as y_1 This term has been found to combine with the doublet term $^2d_2$ and also with the term 1^2s_1 The combinations are as follows —

	y_1 16487 1
$^4d_1$ — 2164 3	18651 4 (1)

	$^2d_2$ 49062 6	1^2s_1 62308 0
y_1 16487 1	32575 4 (2)	45821 7 (1*u*)

Shenstone has derived this term from a consideration of the combinations which occur in the ultra violet region The anomalous behaviour of this term and of the term x_2 which has already been mentioned has suggested that some of the rules which have been found to be so generally valid for the spectra of other elements do not hold for some of the terms of copper

Other Combinations

The following combination has been observed between the two ^2d terms and the old doublet f level

		$^2d_2$ 49062·6	(2042·9)	$^2d_3$ 51105·5
$^2f_{3,4}$	6880·9	42181·8 (4)		44224·5 (2)

It will be observed that the intensities of the lines in this doublet are not in the correct order for a $^2d - {}^2f$ combination, and it is possible that the term 6880·9 does not actually represent a doublet f level. The magnetic resolution shown by the line λ 2369·87 has been observed and the separation is somewhat larger than would be expected for the combination $^2d_2 - {}^2f_3$.

A number of further combinations with the doublet d terms have been noted in the ultra-violet region of the copper spectrum. As Zeeman effects have not been observed for the lines in question, no very definite suggestions are offered as to the nature of the derived terms. The wave-numbers and terms are indicated below

		$^2d_2$ 49062·6		(2042·9)	$^2d_3$ 51105·5	
A	12925·1	36137·6	(8)		38180·3	(10)
B	7523·9	41538·7	(5)		43581·7	(8 R)
C	5964·2	43098·4	(3)		45141·6	(6 R)
D	5657·2	43406·2	(4)		45447·5	(6 R)
E	3031·2	46031·4	(3)		48073·7	(4 U)
F	1714·6	47348·0	(2)		49389·8	(5 R)

The above relations have been previously noted by Shenstone, and he has suggested that the term 12925·1 is a p term. It is possible that some of these terms may be doublet f terms.

The magnetic resolution shown by the strong line λ 2961·18 has been observed but the type has not been identified by the writer. Shenstone has suggested a combination with the term 51105·5, thus :—

		$^2d_3$ 51105·5
G	17345·1	33760·4 (6)

Unclassified Lines of Copper

While the results of the foregoing analysis have led to a considerably clearer understanding of the complex nature of the copper spectrum, there still remains a number of strong lines, the structure of which has not definitely been determined The work of Shenstone has indicated a possible connection between some of these lines and the larger quartet terms presented in the present paper In his letter to 'Nature,' a number of terms are indicated having rather large negative values, and some of those terms combine with the quartet levels of Table II It was hoped that a study of the Zeeman effects would lead to a clearer understanding of the nature of these combinations, but it has been found that, while many of the lines are themselves moderately sharp, the Zeeman effects present such a diffuse appearance that it has not been possible to obtain accurate measurements of them It seems improbable that many of these lines will be classified as quartet multiplets as none of the well-known and easily resolved Zeeman types common to a quartet system appear It may be that some of the negative terms are sextets though no very definite evidence has been adduced in favour of this view

Discussion

The discovery of quartet terms in the arc spectrum of copper is of considerable interest in that it is the only element in the first group of the periodic table whose spectrum has been shown to contain terms of multiplicity higher than two This constitutes a violation of the rule, formerly believed to be generally valid, that the maximum multiplicity of the terms appearing in the spectrum of an element was 1 greater than the group number of the element in the periodic table It seems doubtful, therefore, whether the rule as stated has any very real theoretical significance The question is also raised as to whether the previously held ideas concerning the atomic structure of copper are correct The most recent theories as incorporated in Bohr's table of atomic structures would indicate that the atomic configuration of copper is very similar to that which obtains for the alkali metals The spectra of the alkali metals are known to contain remarkably well-developed doublet series, and the number of unclassified lines is so small as to make it very improbable that there are any quartet terms involved The spectra of the elements of the subgroup Cu, Ag, Au also contain doublet systems, but the series are by no means as complete and the number of unclassified lines is much greater Further, the existence of negative terms and of primed terms in the arc spectrum of copper makes it reasonable to suppose in accordance with recent theories[*][†][‡] that more than one electron is concerned in some of the transitions whereas in the spectra of the alkali metals the frequencies of the lines are believed to be due to transitions of a single valence electron The atomic structure of copper as given by Bohr consists of three full rings with a single valence electron It appears somewhat doubtful whether such a simple arrangement of orbits can explain the evident complexity of the copper spectrum though the arrangements of orbits which give rise to the higher multiplicity terms are not known with certainty

[*Note added February* 3 1926 —It is of interest to compare the results of the present investigation with the recently published theoretical work of Hund[§] The terms derived by Hund for the copper arc spectrum are a ${}^2d$ term which according to his theory should be the largest term and a number of other doublet and quartet terms namely ${}^4p$ ${}^4d$ ${}^4f$ and ${}^2p$ ${}^2d'$ ${}^2f$ It is well known that the largest term of Cu I is a ${}^2s$ term a fact which Hund fails to explain The other theoretical terms however show excellent agreement with experimental data The large d term and the terms ${}^2p$ and ${}^2f$ were previously known and the terms ${}^4p$ ${}^4d$ ${}^4f$ are given in the present paper No ${}^2d$ terms have as yet been identified but it is possible that such terms may be found among the unidentified terms which combine with the ${}^2d$ level]

Summary

A series of observations of the magnetic resolutions shown by copper arc lines has led to the identification in the spectrum of copper of a number of quartet terms The combinations between the quartet terms give rise to a number of multiplets and combinations also occur between some of the quartet terms and the previously determined doublet levels

The relations involving the inter combination lines as has already been pointed out by Shenstone has made it possible to calculate the numerical values of the quartet terms and it has been found that some of these terms must be given negative values

The discovery of quartet terms in the arc spectrum of copper is the first instance in which the spectrum of an element occurring in the first group of

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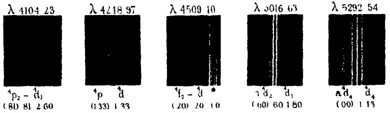
[*] Russell and Saunders Science vol 59 p. 50 (1924)

[†] Wentzel Phys Zeit vol 25 p 182 (1924)

[‡] Millikan and Bowen, Phys Rev vol 26, No 2 (August, 1925)

[§] Hund, Zeit f Phys vol 33 p 341 (1925)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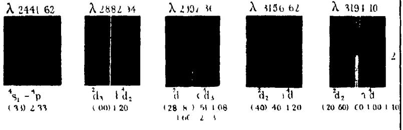
λ 4218 97
λ 4509 10
λ 5016 63
λ 5292 54
$^4p_2 - {}^4d_1$
(81) 81 2 60
^4p ^4d
(133) 1 33
$^4f_2 - {}^4d$
(20) 20 10
$^4d_2$ $^4d_1$
(60) 60 1 80
a $^4d_4$ $^4d_4$
(00) 1 13

1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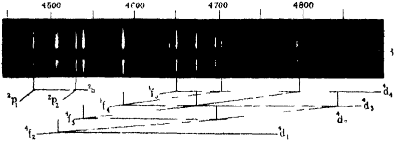
λ 2882 34
λ 2392 36
λ 3156 62
λ 3191 10
$^4s_1 - {}^4p$
(33) 2 33
$^2d_3$ $^4d_2$
(00) 1 20
^2d $^4d_3$
(28 8) 51 1 08
1 60 2 3
$^2d_2$ ^4d
(40) 40 1 20
$^2d_2$ ^4d
(20 60) 60 1 00 1 10

2


4500
4600
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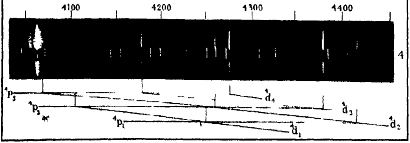
$^2p_1$
$^2p_2$
^2s
$^4f_5$
$^4f_4$
$^4f_3$
$^4f_2$
$^4d_4$
$^4d_3$
$^4d_2$
$^4d_1$

3


4100
4200
4300
4400
$^4p_3$
$^4p_2$
$^4p_1$
$^4d_4$
$^4d_3$
$^4d_2$
$^4d_1$

4

the periodic table has been shown to contain terms of multiplicity higher than 2 This constitutes an exception to the rule that the maximum multiplicity of the terms in the spectrum of an element is 1 greater than the group number of the element in the periodic table The knowledge of the existence of quartets in the copper spectrum further raises the question as to whether the previously held ideas concerning the atomic structure of copper are correct

The work outlined in this paper has been done at the Imperial College of Science and Technology under the direction of Prof A Fowler F R S The writer wishes in concluding the paper to express his appreciation of the opportunity which has been given him for carrying out the experiments, and to thank Prof Fowler for the interest which he has taken in the work

DESCRIPTION OF PLATE 8

1 Photographs of *Zeeman effects shown by quartet combinations of copper* The photograph of the line λ 4509 40 includes the pattern of the silver line λ 3382 86 which is marked with an asterisk

2 *Zeeman effects of inter combination lines* (*Error*.—For $^4s_1$ $^4p_1$ read $^2s_1$ $^4p_1$)

3 —Copper spectrum λ 4450–4900 with iron arc comparison, showing $^4f\,^4d$ multiplet The scheme of the multiplet has been indicated in the very convenient way suggested by Meggers The horizontal and oblique lines represent the terms of lower and higher azimuthal quantum number respectively The lines corresponding to the various combinations are indicated at the intersections of the lines

4 Copper spectrum λ 40 0 45 0 with iron arc comparison showing $^4p\,^4d$ multiplet The same scheme is employed as in 3

The Controlling Factors of Transfer Resistance

By Edgar Newbery, D Sc, F I C University of Cape Town

(Communicated by Sir Ernest Rutherford O M, Pres R S --Received January 9, 1926)

(Plate 4)

In a previous communication* by the author, it has been shown that the application of the cathode ray oscillograph to the problem of electrode potential provides direct evidence as to the reality of transfer resistance This work has been continued with a view to obtaining further information upon the subject of transfer resistance

Experimental - The apparatus used was the same as that previously described, with the exception of the following small modifications -

1 The potentiometer P was replaced by two standard Weston cells, and the switch S_2 by a four way switch arranged so that potential differences of 0, 1, and 2 volts could be applied between the filament and grid of the valve V after the potential curve of the cathode C had been traced out

2 The sliding rheostat R_3 was replaced by a fixed frame resistance, as a troublesome "wandering" of the oscillograph beam was traced to minute variations in the filament current, produced by variations in the resistance of the sliding contact It is possible that some of the earlier measurements are slightly in error from this cause

3 The resistance R_4 was increased from 150,000 ohms to 500,000 ohms

4 The use of very rapid plates (Barnet orthochromatic special sensitive) enabled the time of exposure to be cut down to 10 secs for the curve and 2 secs for each of the comparison spots

5 For preliminary observations and rough estimations, a ruled glass screen was placed against the oscillograph screen, and weakly illuminated through the edge of the glass by a small 4-volt lamp Rough measurements could thus be taken without photographing

The factors studied in the present work are (1) material of electrode, (2) surface of electrode, (3) current density

Other factors which the author hopes to investigate shortly are time, temperature, addition agents, change of electrolyte, anodic phenomena, etc

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* 'Roy Soc Proc ' A, vol 107, p 486 (1925)

The electrodes used—copper silver gold nickel and platinum—were chosen on account of their capacity for taking a high polish as previous work had indicated that this was one of the factors producing a high transfer resistan All were in the form of plates 1 cm square supported vertically in the electrolyte (N H_2SO_4) and having the back edges etc insulated with a coating of hard white sealing wax The polishing was effected by means of various grades of emery paper from 0 to 0000 followed by a final burnishing with an agate burnisher After a series of photographs had been taken with the electrodes in this condition they were rubbed with No 0 emery cloth and a corresponding series taken the results being given under the titles polished and rough

The current densities given are the actual readings of the amperemeter Since the current was only flowing for half the time of revolution of the commutator the real current density while the current was flowing was double the value given In calculating transfer resistance this doubled value is utilised

In all cases the commutator was revolved at a uniform rate of 200 revolutions per minute

Some of the curves obtained are given in figs 1–6 (Plate 4) and the values of the over voltage and transfer resistance calculated from measurements on these curves are given in the following table —

Column A — Current density in milliamperes per square centimere
B Over voltage in volts
C — Transfer resistance in ohms per square centimetre

	A	B	C
Copper polished	1	0 35	25
	10	0 35	10
	100	0 35	4 2
	1000	0 4	0 77
Copper rough	1	0 35	—
	10	0 35	5
	100	0 35	3
	1000	0 4	0 77
Copper rough {in N H_2SO_4 + N/10 $C\ SO_4$	10	0 35	0 0
	100	0 35	
Silver polished	1	0 25	65
	10	0 25	23
	100	0 2	5 7
	1000	0 2	0 8
Silver rough	1	0 25	35
	10	0 25	16
	100	0 2	6 7
	1000	0 2	0 8
Silver rough in 10 N H_2SO_4	10	0 25	13
	100	0 2	3

Table—*continued*

	A	B	C
Gold polished	1	0 25	50
	10	0 25	16
	100	0 25	4
	1000	0 2	0 9
Gold rough	1	0 25	
	10	0 25	10
	100	0 25	2
	1000	0 2	0 7
Nickel polished	1	0 25	60
	10	0 25	15
	100	0 3	5
	1000	0 3	0 8
Nickel rough	1	0 2	25
	10	0 25	11
	100	0 25	4
	1000	0 3	0 7
Platinum polished	1	0 05	40
	10	0 05	12
	100	0 0	5
	1000	0 0	0 8
Platinum rough	1	0 0	—
	10	0 0	3 5
	100	0 0	4
	1000	0 0	0 8
Platinum platinised	100	0 0	2
	1000	0 0	0 8

Discussion of Results —From the data given in these tables it will be at once evident that over voltage and transfer resistance are two entirely different independent quantities with quite distinct sets of controlling factors

Over voltage appears to be nearly a constant and definite quantity for each metal and is but little affected by concentration of electrolyte current density or mechanical condition of the surface

Transfer resistance on the other hand, appears to be independent of the chemical constitution of the electrode but is strongly affected by the mechanical condition of the surface and most of all by the current density So great is the influence of this last factor that at high current densities the transfer resistance at all the electrodes is practically the same At low current densities, transfer resistance may rise to high values, more specially when the electrode is highly polished No upper limit has been found and it is probable that transfer resistance approaches infinity as the current density approaches zero The higher values are, of course, increasingly difficult to measure with any accuracy from the curves

From consideration of these results, together with previous work on the same subject, the author is of opinion that in future over-voltage must be looked upon as essentially a chemical phenomenon transfer resistance as a physical or mechanical

Accuracy of the Method —Owing to the discovery and elimination of certain small errors in the original apparatus the values in the present work are probably more accurate than those previously given Many more observations have been taken than are actually listed and the variations found to be negligibly small under definite conditions In particular the over voltages of copper and nickel given in the present work as 0 35 and 0 25 volt respectively are more reliable than the values 0 5 and 0 4 previously given the error being due to the wandering of the beam already referred to

The sensitivity of the method for detecting very rapid but continuous changes of potential may be estimated from a slight mechanical defect in the apparatus The resistance R_7 controlling the current through the solenoids S consisted of a platinum wire nearly but not quite encircling an ebonite drum The length of the gap between the ends of this wire was 2 mm and when the platinum brush was in this gap the spot took up the position shown in most of the prints as a somewhat faint mark in line with the reference spots Since the circumference of the drum was approximately 300 mm and the speed of revolution 200 per min the time available for this mark to be made was 0 002 sec This is however far from the limit available When the screen is viewed in the dark room by an eye rested in the dark for a few minutes a complete horizontal line of light is seen joining the spot just described with the main curves This line is almost invisible in the prints but is more clearly seen in the negatives and could be reproduced if necessary by longer exposure of the plate and printing on soft paper It is caused by the tiny spark produced on breaking the solenoid circuit (1 ampere at 2 volts) and indicates that this break is not instantaneous Careful observation of this spark showed that its length did not exceed 0 1 mm and since the time taken for the drum to rotate this distance is 0 0001 sec and the length of the line is approximately 2 5 cm we may conclude that the spot of light will leave a perfectly clear and definite trace if it travels over the screen at the rate of 25 000 cm per sec In many of the photographs, for example the distance between the upper and lower sections of the curves is several mm , and no trace of any line joining the two sections could be detected by the most careful inspection Hence the time taken for the first fall of potential of the cathode after breaking the charging circuit, must be very small compared with one hundred thousandth part of a second It is evident that such a rapid change of potential must be produced by the removal of a passive ohmic resistance, and not by changes in an active electro motive force produced by ionic concentration surface tension etc

The limits of error in measuring actual over-voltages and transfer resistances by this method are unfortunately rather wide and the apparatus is far from perfect The spot of light is too large for accurate measurements and it is difficult to prevent it changing its size and shape during an experiment. The correct adjustment of the solenoids is also a matter of some difficulty, and in many of the photographs the line of the curves is not truly at right angles to the line joining the reference spots Also the potential difference-current curve of the thermionic valve is not a straight line, and hence the distance between the reference spots denoting 0 and 1 volt is less than that between those denoting 1 and 2 volts

Hence no greater accuracy can be claimed for over-voltage values by this method than ± 0 05 volt

In measuring transfer resistance at high current densities the limits are well within ± 0 1 ohm but at low current densities the error may easily exceed 10 ohms In some cases the uncertainty is so great that no estimate has been given at the lowest current density used Thus in the case of platinised platinum the curves obtained at the two lowest current densities were so nearly continuous straight lines that it was considered unnecessary to reproduce them

Theory of Transfer Resistance.—It is well known that when a small E M F is applied to a pair of non-attackable electrodes in dilute acid, a sudden rush of current occurs which rapidly falls to nearly zero This rush of current is undoubtedly caused by the discharge of ions at the electrodes with formation of a film of gas on the surface, the small "residual current" merely serving to replace the few ions escaping from the electrode by diffusion Repeated small increases in the applied E M.F produce similar effects, but the residual current increases each time until visible gas evolution occurs When this state is arrived at, the whole surface must be saturated with gas, and there must therefore be a continuous film of gas over the entire surface If it were not so, any bare spot on the surface would be at a lower potential than the surrounding areas, and a rush of ions to that spot would at once cover it with gas Owing to surface-tension forces, this film of gas requires an appreciable time to collect into bubbles large enough to break away from the electrode, but in the meantime more ions are showering on to the same electrode under the influence of a force which varies inversely with the square of their distance from that electrode The film is therefore subjected to enormous pressure, and whenever it breaks down under this pressure it is instantly re-formed by freshly discharged ions. In other words, the film offers resistance to the passage of the current-carrying ions, and this resistance is transfer resistance.

It is now evident that a rough surface will show a lower transfer resistance than a smooth one, since the formation of bubbles and escape of gas will be greatly facilitated by the numerous points projecting into the electrolyte

It is not so easy to understand why transfer resistance is so greatly diminished by increase of current density It might be thought that the film of gas would become thicker and the resistance increase as the current density rose, but the curves obtained show that, although the film may or may not increase in thickness, its resistance undoubtedly decreases--that is to say, it becomes more conducting under the influence of higher electrical pressure The exact mechanism of this change is doubtful, but it is possibly due to diminution in thickness of the gas film due to the high pressure exerted by the attractive force of the charged cathode acting upon the charged ions on the opposite side of the gas film It is possible also that under the influence of the intense electric field existing across the film, electrons may be discharged through the film on to the ions outside, thus liberating gas in the body of the liquid and to some extent relieving the pressure on the electrode surface This latter supposition is the more probable in view of the fact that over-voltage usually falls (sometimes to nearly zero) at very high current densities Glasstone* has recently suggested that transfer resistance is caused by a "diffusion layer" over the surface of the electrode, due to exhaustion of hydrogen ions in the liquid immediately surrounding the cathode There is little doubt that this effect has some influence upon the magnitude of the transfer resistance, but the relative importance of such influence is open to question In the case of metal deposition from neutral electrolytes when no gas is liberated, it may be responsible for the whole of the transfer resistance, but previous work by the author† seems to indicate that in such cases transfer resistance is very small Glasstone's theory would locate the source of transfer resistance in the electrolyte, and it is difficult in this way to account for the observed influence of roughening of the electrode surface Again, the great lowering of transfer resistance with rise of current density is still more difficult to account for

In order further to test this theory, two series of experiments were carried out In the first series, sufficient copper sulphate was added to the sulphuric acid electrolyte to render it tenth normal with respect to copper The surface layer at a copper cathode in such a solution would be rapidly exhausted of the slow speed copper ions, and, according to Glasstone's theory, the transfer resistance should therefore be almost unaffected Experiment shows that this is far from the case (see figs 5 and 6 Plate 4) At comparatively low current densities transfer resistance is reduced to zero and at higher current densities when considerable quantities of hydrogen are liberated along with the copper the transfer resistance is greatly reduced over voltage being unchanged in either case

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* 'J. Chem Soc,' vol. 127, p. 1824 (1925)

† 'Trans Far Soc.,' vol. 15, Part I (1919)

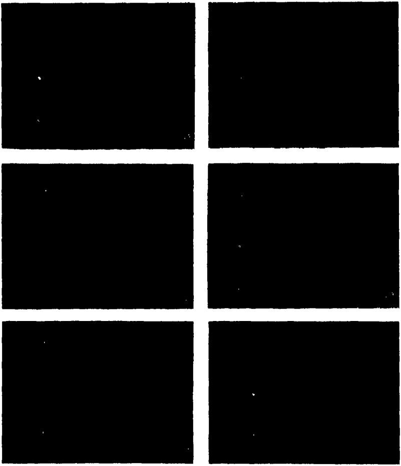
In the second series the concentration of the electrolyte was varied According to Glasstone s theory transfer resistance should be almost inversely proportional to concentration of electrolyte A series of observations with a rough silver cathode in tenth normal normal and ten normal sulphuric acid gave the following results

Current density milliamperes per square centimetre	1	10	100
Transfer resistance in —			
Tenth normal acid	35	16	12 ohms
Normal acid	35	16	5 7
Ten normal	30	13	3

The over voltage was the same in all three solutions

These results show that at low current densities transfer resistance is but little affected by concentration changes in the electrolyte but at high current densities the effect is great It appears therefore that transfer resistance is itself a complex quantity made up of at least two parts one due to a gas film which is greatly affected by changes of current density and another due to Glasstone s diffusion layer which is but little affected by such changes At low current densities the former is overwhelmingly great but at high current densities it tends to disappear whilst the latter becomes more prominent The separate estimation of these two effects is a problem of some difficulty

The stirring effect of gas bubbles mentioned by Glasstone cannot account for the great fall of transfer resistance as the current density is increased since this effect is observable though to a smaller degree during metal deposition when no visible gas bubbles are produced It is probable that local heating across the diffusion layer has a considerable effect in lowering this part of the transfer resistance but the most powerful influence at work is undoubtedly the very intense electric field across the gas film Although the actual fall of potential across this film may not exceed one volt the film is so thin that the potential gradient is enormous and the internal friction very small Hence the chances of electrons shooting right through the film without collision are great and at high current densities the electrical resistance of the gas film may become



negligibly small nearly the whole of the transfer resistance being then accounted for by the diffusion layer

N D Holler * using an apparatus similar to that employed by the author concludes that transfer resistance is due to a gas film

Summary

The variations of transfer resistance due to condition of electrode surfaces and changes of current density have been investigated with the five metals copper silver gold nickel and platinum

Transfer resistance is almost independent of the chemical nature of the electrode but is high with polished surfaces and low current densities and low at rough surfaces with high current densities

At very high current densities transfer resistance is very low and nearly independent of the nature and condition of the electrode surface but is greatly affected by changes of concentration of the electrolyte

Transfer resistance is made up of two parts (1) the resistance of a film of gas over the electrode surface (2) the resistance of a layer of partially exhausted electrolyte surrounding the electrode

The fall of transfer resistance at high current densities is due to the increase of conductivity of the gas film under the influence of a high potential gradient

Over voltage is essentially a chemical transfer resistance a physical phenomenon

EXPLANATION OF PLATE 4 (see Table pp 183 4)

Fig 1 —Copper polished Current density 1
Fig 2 —Copper polished Current density 100
Fig 3 —Copper rough Current density 1
Fig 4 —Copper rough Current density 100
Fig 5 —Copper rough (in $N\ H_2SO_4 + N\ 10\ CuSO_4$) Current density — 10
Fig 6 —Copper rough (in $N\ H_2SO_4 + N\ 10\ CuSO_4$) Current density — 100

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* Bureau of Standards Sci Paper No 504

Evidence for a Film Theory of Hydrogen Overpotential from Surface Tension Measurements

By A L McAulay, F Inst P , Ph D , and F P Bowden, Jnr , B Sc

(Communicated by Prof F G Donnan, F R S —Received January 16, 1926)

I – *General*

Whenever hydrogen overpotential occurs at a cathode there must be some transition layer between the electrode surface and the electrolyte, where hydrogen exists in a condition whose free energy is greater than that of the gaseous hydrogen into which it passes Even if the overpotential is believed to be the result of a resistant film this point of view is still applicable, the additional free energy in this case being the electrical energy between the plates of a condenser

The experiments described below seem to show that this layer has many of the properties of a skin or film, and it will be referred to in the future as a film, without any significance being attached to the term besides that deduced in the course of the discussion

The experiments to be described were undertaken with the object of investigating the nature and properties of this film, and consist mainly of simultaneous observations of the single electrode potential and the surface tension under varying conditions, at a mercury cathode at which hydrogen is being evolved These observations were made with a pure acid electrolyte and also with metal ions in solution with different current densities

The results obtained indicate that a film of high surface tension must form over the mercury surface before hydrogen can be liberated, and that this film persists after the current depositing the hydrogen is stopped and the overpotential has disappeared, provided that the electrolyte is of pure acid The presence in the electrolyte of metal ions less noble than copper does not hinder the production of the film nor destroy it when produced, but the presence of metal ions more noble than copper does prevent the formation of the film at low current densities and destroys it instantly on open circuit.

The indication is that overpotential is a secondary effect caused by a tangible film hindering the transformation of hydrogen ions into gaseous hydrogen

2 *Experimental Arrangement*

In most of the experiments the cathode was a surface of mercury in a vertical tube of 3·5 mm diameter The electrolyte filled the tube above the mercury to overflowing and an anode generally a platinum wire dipped into the top

The surface tension measurements were made by observing the changes in height of the mercury meniscus on an eyepiece scale in a microscope The absolute values of the surface tension changes observed are only to be taken as rough as the angle of contact of mercury and glass in the presence of the solutions used was not known The value assumed throughout was 52°

The measurements of single electrode potential were made by means of a fine drawn glass tube with a tip of about 0·1 mm diameter which passed down through the electrolyte to within a fraction of a millimetre of the mercury A slow flow of solution was passed through this tube to prevent bubbles from entering and blocking it In spite of the movement of the mercury due to changes in surface tension ohmic effects were only troublesome at very high current densities The potential measurements were made in the usual way on a potentiometer against a calomel electrode

Experiments were also made using as a cathode a pool of mercury and weighing before and after passing current to determine the proportions of metal and hydrogen deposited under varying conditions

3 *Experiments on Production of Overpotential Film in Solutions containing Noble Metal Ions*

Fig 1A shows a typical curve connecting current density with single electrode potential and fig 1B a curve connecting current density with surface tension

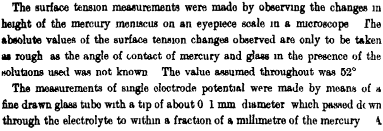

Fig 1A Fig 1B

Electrolyte N/1 HNO_3 + N/10 $HgNO_3$

Current Density in Amps /Cm²

Single Electrode Potential in Volts on Calomel Scale

Change in Surface Tension in Ergs/Cm²

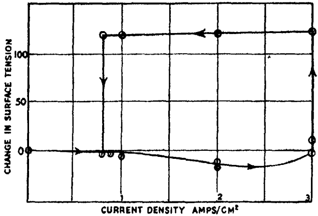

Fig 1c

Electrolyte N/1 HNO_3 + N/10 $AgNO_3$
Current in Amps /Cm² Change of Surface Tension in Ergs/Cm²

the electrolyte being normal in HNO_3 and 0 1 normal in $HgNO_3$ Fig 1c shows results obtained with an electrolyte normal in HNO_3 and 0 1 normal in $AgNO_3$ The general nature of the phenomena is the same in both cases though the results differ in detail

Consider first the case of HNO_3 containing $HgNO_3$ (figs 1A and 1B) For current densities of less than 0 02 amp /cm² the potential remains very near the reversible value for mercury and the surface tension changes very little At higher current densities both potential and surface tension begin to fluctuate over small limits The period of the fluctuations in the particular experiment the progress of which is being considered was about a second, but it may vary over wide limits There is some evidence that this fluctuation is due to an alteration of the mercury salt between the mercurous and mercuric states

At this stage no hydrogen is being liberated As the current density is increased a point is reached where the conditions instantaneously alter, hydrogen is evolved, the surface tension rises more than 100 ergs/cm² and the potential of the cathode becomes more than 1½ volts more negative The film is established. In this condition a more or less large proportion of the current is still carried by mercury as proved by weighing the cathode The transition to this state occurs as far as can be determined instantaneously, the determining factor being apparently the accumulation of hydrogen ions In the case of the experiment graphed the transition occurred at a rather unusually low current density, after this current had been running for about five minutes It would have been easy to reach a current density of 0 3 amp /cm.^{2} before the transition occurred by making the transition rapid Vigorous stirring hinders the transition but will not destroy the film once it is established

Fig 1c shows the surface tension current diagram for a corresponding experiment using N/10 $AgNO_3$ in place of $HgNO_3$ The progress of the experiment is represented by the arrows For current densities greater than about 0 2 amp /cm.^{2} the mercury surface was thrown into rapid vibration This vibration was very much more rapid and of quite a different type from the variation in surface tension referred to above

At the current density of 0 3 amp /cm ^{2} the transition occurred, the electrode potential being in this case about -1 3 volts On decreasing the current density the film remained intact until, a few seconds after it had been lowered to 0 08 amp /cm ^{2}, the reverse transition occurred, the potential falling to between $+0$ 3 and $+0$ 4 volt

The only characteristic differences between the two experiments described are the variations of surface tension and potential that occur with mercury in solution and not with silver, and the rather higher overpotential obtained with mercury All the other differences are non-essential and depend on the precise way in which the experiments are conducted

Accompanying the transition from the negative condition with high surface tension, a remarkable change takes place in the character of the bubbles that have formed on the surface From a condition in which they are flat and appear clamped to the surface of the cathode, disengaging themselves only with difficulty, they suddenly become spherical and almost free of the surface A large proportion actually comes away as the mercury column rises. An obvious explanation is that the film does not exist between cathode and bubble, and that therefore the gas will endeavour to spread over the mercury as far as possible when the film is established

When salts of the following metals (Na, Zn, Cd, Fe, Co, Sn, Pb, Sb) are added to an electrolyte when the overpotential film has been formed, no change in the surface tension takes place With salts of the following metals (Ag, Hg, Au, Pt, Ir) the surface tension decreases instantaneously by an amount of the order of 100 ergs/cm ^{2} With a Cu salt a lowering of surface tension of the order of 20 ergs/cm ^{2} is observed

Theory —The experiments described in this section are consistent with the following theory An adsorbed film must be formed over the surface of the cathode before hydrogen can be evolved This film has a high surface tension

It has a place in the electrochemical series more positive than H and near but slightly more positive than Cu It is immediately replaced by ions more noble than Cu if they are present in the electrolyte This theory will be taken as a basis for discussion and in the next section further experiments will be described, made with a view of studying the nature and properties of the film in more detail

4 *Overpotential Film in Solutions which do not contain Noble Metal Ions*

Fig 2 shows curves connecting single electrode potential with current density for electrolytes of pure acid and of acid, and salts of metals less noble than silver The curve for silver is added for comparison

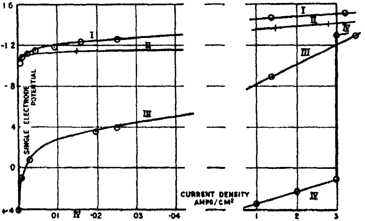

Fig 2 —Electrolytes Curve I—N/1.HNO$_3$ Curve II—N/1 HNO$_3$ + N/10.Zn(NO$_3$)$_2$ Curve III—N/1 HNO$_3$ + N/10 Cu (NO$_3$)$_2$ Curve IV—N/1 HNO$_3$ + N/10 AgNO$_3$. Single Electrode Potential in Volts on Calomel Scale

Fig 3 shows the corresponding curves connecting surface tension with current density

Fig. 4 shows the result of another experiment where electrolysis was started in pure acid with very much smaller current densities and the rise of surface tension was observed Both single electrode potential and surface tension are plotted In all cases the equilibrium value is plotted, for the smallest current density (1 × 10^{-5} amps) three minutes were required for the rise to take place, and other experiments show that a very slow rise continues for at least an hour With higher current densities equilibrium is reached almost immediately

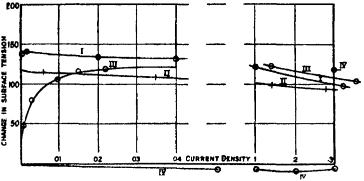

Fig 3 Electrolytes the same as in Fig 2 Change in Surface Tension in Ergs/Cm ^{2}

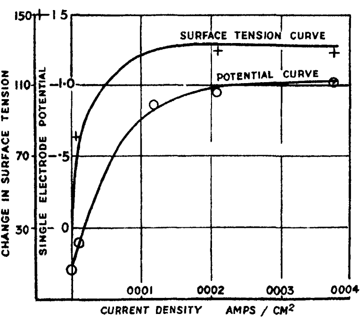

Fig 4—Electrolyte N/1.HNO$_3$ Vertical Scales—Change in Surface Tension to 150 Ergs/Cm ^{2}; Single Electrode Potential to — 1 5 Volts (Calomel Scale)

The conditions in the absence of noble metal ions are seen to be completely different from those obtaining when these ions are present The film is established by extremely small currents The surface tension rises very rapidly with current density, and thereafter remains at an almost constant value, dropping slightly as the single electrode potential increases, as would be expected of a surface receiving increments of charge Instead of the film being destroyed when the circuit is broken it remains intact with a rather higher surface tension than when current was flowing The single electrode potential, however, falls considerably If the apparatus is allowed to stand for a few hours on open circuit the surface tension falls to its original value

Although the film is destroyed by standing for some time it is extremely difficult to destroy artificially without the addition of noble metal ions Removing and renewing the solution does not affect it, adding mercury to the top of the column and even removing part of the mercury and pouring it back again leaves the surface tension high and the electrode potential negative

On the other hand, the trace of a salt of a noble metal destroys the film immediately, and sometimes it disappears rapidly with time The case of Cu is somewhat anomalous throughout, but it is much more nearly akin to that of Zn than to that of Ag Further consideration will be given to this point later

Theory —The following theory is consistent with the above facts The overpotential film forms extremely easily in an acid solution, and once formed remains unless replaced by ions more electropositive than itself Mercury ions are very slowly detached from the mercury (the film not being protective), and go into solution in the acid After a time the concentration of these is sufficiently great to replace the film, and it is destroyed The overpotential is due to the resistance offered by the film. The effect of this is probably twofold First, there is something in the nature of an ohmic resistance, and next electrochemical processes are hindered, resulting in a layer of high free energy, which to some extent dissipates itself, although the film remains intact when the circuit is broken

It was felt that though the above theory accounts for the facts, the evidence for the direct connection between the extra surface tension (which must be looked on as the direct effect of a film) and the overpotential was not sufficiently strong This evidence has come so far from such experiments as those whose results are shown in fig 1, where the abrupt changes of overpotential and surface tension invariably occur together, and in experiments with pure acid electrolyte and low current densities where the rise of surface tension and of single electrode potential with time are always found to take place together.

The experiments described in the next section were made with the object of establishing the fact that the presence of the film makes possible the production of overpotential under conditions that would otherwise not produce it

5 *Effect of Film on Establishment of Overpotential*

With a pure acid electrolyte a current density of 1×10^{-5} amps /cm ^{2} was passed through a mercury cathode for 77 minutes In that time the single electrode potential changed from + 0 368 to + 0 010 on the calomel scale the surface tension of the film on the mercury changing from 10 ergs/cm ^{2} to 83 ergs/cm ^{2}

This current flowing for more than an hour was not capable of producing an overpotential A film was next formed by passing a current of density 1 amp /cm ^{2} for a few minutes The circuit was then broken for 43 minutes, at the end of which time the electrode potential was + 0 011, but a film was established, the surface tension being 180 ergs/cm ^{2}

On now passing a current of density 1×10^{-5} amps /cm ^{2} the single electrode potential became much more rapidly negative than in the previous experiment, reaching a value of − 0 456 in 7 minutes, *i e*, in 7 minutes it had produced an overpotential of 0 170 volt

These experiments would appear to provide strong evidence in favour of the theory outlined at the end of the two preceding sections by showing directly that the presence of the film favours the production of overpotential

6 *Relation between Surface Tension and Single Electrode Potential*

Fig 5 shows a curve connecting surface tension and single electrode potential, obtained by the use of very small current densities with pure acid electrolytes Such experiments indicate that for electrode potentials more positive than about − 0 05 volt on the calomel scale, the potential is a single-valued function of surface tension, and that these quantities are connected by a straight line law Neither statement is true above this potential, the single electrode potential rising rapidly, while the surface tension soon becomes nearly constant. Also the relation does not hold for films established by higher current densities In these cases higher surface tensions are obtained on open circuit

The graph shows that with the above qualifications the potential difference above + 0·42 volt bears a constant ratio r to the surface tension The value of this ratio is about 0 0040 This ratio remains constant up to surface tensions of 110, but a glance at figs 2 and 3 shows that with current densities of only about 0 0001, and surface tensions of about 130, *r* is as high as 0 009, and becomes higher for larger-current densities By passing a large current, and then breaking the circuit, values of *r* of about 0·009 are obtained with potentials up to —0 9 Nearly always the surface tensions are over 120 in such cases, but on one occasion by adding fresh mercury to the cathode directly after passing a large current, a value of *r* was obtained on open circuit

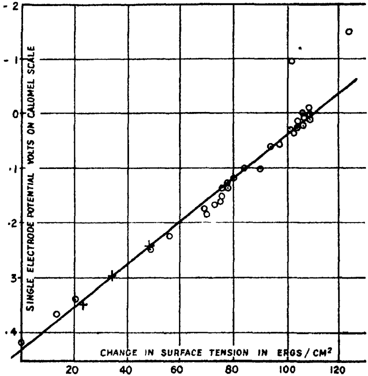

FIG 5 —Electrolyte: N/1.HNO_3.

of 0 0098 with a surface tension of only 61 ergs/cm.². High values of *r* have never been obtained with potentials more positive than — 0 05 volt

With the electrode potential rendered negative on open circuit by previous passage of a large current an experiment was made to investigate the change in surface tension produced by making the electrode positive artificially by means of an applied electromotive force The results are shown plotted on fig 5 as crosses

Theory.—The following theory is consistent with the above experiments. The film is produced as the result of the accumulation of hydrogen ions brought up to the cathode by the current. Its surface tension increases as it is built up. At the commencement of the action the solution pressure, P, is given by

$$0{\cdot}98 \times 10^8 = \frac{RT}{9647} \log \frac{1{\cdot}1 \times 10^8}{P},$$

$0{\cdot}98 \times 10^8$ being the absolute potential of $+0{\cdot}42$ volt on the calomel scale and $1{\cdot}1 \times 10^8$ the osmotic pressure of the ions in a normal solution. Until the film attains this solution pressure the single electrode potential will remain at the value characteristic of mercury in that particular electrolyte. Further passage of current causes further accumulation of ions and builds up the film giving it greater surface tension and a higher solution pressure. This is supported by the fact that Cu ions when in solution replace a part of the film produced by a high current giving a sudden drop in surface tension on breaking circuit similar to that obtained with Hg or Ag ions but much smaller in magnitude. This drop is absent with all ions more electronegative than Cu. The point at which r increases may correspond to a change in condition, possibly the completion of a monomolecular layer, the added material of the film being no longer tightly adsorbed on the cathode surface and causing little increase in surface tension. The free energy of the film, however, continues to increase. On opening the circuit the high free energy does not immediately dissipate itself and the film become gaseous hydrogen, for the same reason that nitro-glycerine does not spontaneously lose its high free energy and explode. The general picture here suggested is consistent with the known fact that the over-potential at almost all cathodes approaches the same value at high current densities.

The over-potential when the polarizing current is flowing is invariably higher than that observed on open circuit, *e.g.*, on breaking the circuit the potential falls extremely rapidly (within one-fifth second) from $-1{\cdot}3$ volts to $-0{\cdot}93$ volt on the calomel scale. Values higher than this have never been obtained on open circuit. The decay from this lower value is slow, in some cases many minutes elapsing before a sensible decrease occurs. From this it would appear possible that part of the over potential measured while the current is flowing is due to the ohmic resistance of the film, which behaves as a leaky condenser

Summary

Simultaneous measurements have been made of the single electrode potential at a mercury cathode, and of the changes in surface tension of the mercury obtained when various currents flowed through different electrolytes

The following conclusions were reached *In order that hydrogen may be liberated at the cathode a film of high surface tension must first be formed over the mercury* In a pure acid electrolyte the passage of extremely small quantities of electricity produce this film, which remains intact when the circuit passing the current is broken

The addition to the acid of small quantities of ions of metals more noble than copper destroys the film completely and instantly The following gave this result, Ag, Hg, Au, Pt, Ir The addition to the acid of ions of metals less noble than copper leaves the film intact The following gave this result, Na, Zn, Cd, Fe, Co, Sn, Pb, Sb The effect of Cu is intermediate between these cases Thus it seems that *the film when fully formed has a definite place in the electrochemical series*

The production of an over potential at the cathode requires the initial establishment of the film Conditions that will *not* produce over-potential when a film has not first been formed over the cathode do produce an over-potential when a film has previously been formed over it

Relation between Single Electrode Potential and Surface Tension.—The film can be built up slowly by the passage of extremely small currents Till a certain stage is reached the single electrode potential measured above the reversible potential of mercury is proportional to the surface tension of the film. Further addition to the film increases the single electrode potential but leaves the surface tension approximately constant

A Note on the Significance of the Electrode Potential

By J Heyrovský, D Sc , Ph D , Charles University, Prague

(Communicated by Prof F G Donnan, F R S —Received February 1, 1926)

The following lines will suffice in this journal to invalidate Mr J A Butler's criticism* of the present author's communication "The Significance of the Electrode Potential"†

1 In the present author's formula the "ionisation potential" expresses correctly the free energy of gaseous ionisation of atoms since there is—at room temperature—no difference between the total and free energy of such ionisation ‡

2 The term Mr Butler proposes for the expression of free energies of hydration§ is included in the writer's symbols $H_{MeOH}\ F$ and $H_H\ F$

3 The "cycle" by which Mr Butler tries to invalidate the present author's formula for the electrode potentials‖ has no bearing upon any electro chemical process In Butler's deduction the negative charges (the electrons) as well as the positive charges (the ions) are brought into the metallic electrode in exactly the same way, viz , from the ionisation equilibrium box I (stage 2, p 669) through the wet surface -inside the cell and solution—into the metallic electrode (stages 3 and 8) Consequently the electrical work (ϕ F) done in crossing with the negative charge the (moist) surface potential ϕ must be equal and opposite to the work ($-E_s\ F - \pi\ F$) done in crossing, with the positive charge, the surface potentials E_s and π Hence, of course, Mr Butler's results follows at once, viz —

$$\pi\ F + E_s\ F - \phi\ F = 0,$$

which condition he should have been able to see immediately without his elaborate and lengthy cycle

Such a treatment, however, cannot lead to any electro-chemical thermodynamic cycle, and this is where Mr Butler is absolutely wrong The present author has nowhere brought electrons over the same interfaces as positive ions , on the contrary, everywhere the transfer of electrons into the perfectly dry metal (outside the cell) was considered, whereas the ions were brought over the wet solution interfaces into the electrode (inside the cell).

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* 'Roy Soc Proc,' A, vol 104, p 667 (1923).

† 'Roy Soc Proc ,' A, vol 102, p. 628 (1923).

‡ See the writer's first reply to this criticism in the 'Chemical News,' vol. 128, p 357 (1924)

§ Butler, *loc. cit* , p 668, 6th line from bottom

‖ *Loc cit.*, pp. 668–670.

It is only the latter mechanism which leads to a differentiation between the electric work terms, expressing the actual charging process of the electrodes, since electrons do not penetrate into solution but pass—during the electrolysis—through the metallic connection outside the cell

Correcting thus Mr Butler's cycle by writing ϕ for the potential difference of the *dry* metal outside the cell and consequently leaving out the work term RT $\log_e \epsilon_s/\epsilon_M$ (in Butler's notation, p 669, 17th line), which expresses the bringing of the electrons through the wet surface into the electrode, we obtain —

$$\pi\ F + E_s\ F - \phi\ F = - RT \log_e \epsilon_s/\epsilon_M$$

Substituting further from the constant

$$K_{Me} = Me^+_s\ \epsilon_s/Me_s = Me^+_s\ \epsilon_M/Me_s,$$

where Me^+_s means the concentration of (unhydrated) metallic ions imagined to exist in equilibrium with the electrode, solution and vapour, ϵ_M the equilibrium concentration of electrons above the wet electrode surface and Me_s ($= Me_M$) the vapour pressure of the metallic electrode, we have —

$$\pi + E_s - \phi = RT/F \log_e Me^+_e/Me^+_s, \qquad (1)$$

an expression quite different from zero *

The present author has shown elsewhere† that his criticised formula‡ for the electrode potential is obtained, by further substitution, from the above expression (1), which coincidence must indeed be expected from thermodynamics, since now both the corrected Butler's as well as the writer's cycles are reversible

Summary

1 It is explained that the stages of the author's cycle, denoted by J A. V. Butler as irreversible, involve the correct free energy terms

2 Mr Butler's proof, that the author's potentials round the cycle are zero, is shown to be faulty owing to Butler's transfer of electrons over the metal-solution-vapour interface instead of bringing them over the dry metallic surface outside the cell When this wrong step is avoided, it leads to the same relation between the electrode potential and the basic and ionisation constants, as has been deduced by the present author, thus furnishing a further proof of the correctness of the deductions made by the latter

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* *Cf* the writer's first reply, 'Chem News,' *loc. cit*, p. 358, and the second reply, *ibid.*, vol 129, p 329 (1924)

† 'Chem News,' *loc cit*, 'Jour Phys Chem,' vol 29, p. 344 (1925); 'Compt. Rend Acad Paris,' vol. 180, p. 1655 (1925)

‡ *Loc cit*, p 631, 8th line

The High Temperature Oxidation of Metals

By J S Dunn, M.A., Ph.D.

(Communicated by Dr W Rosenhain, F R S —Received January 28, 1926)

The oxidation of metals at high temperatures has been investigated with some thoroughness by Pilling and Bedworth * They found that the metals could be divided into two great classes according to the nature of the oxide produced. If the volume of the oxide is greater than that of the metal from which it was produced an oxide film of compact structure and protective properties will be produced If the volume of the oxide is less than that of its parent metal a porous oxide is produced which has no protective action whatever

The oxidation of the metals of the first class is controlled by the diffusion of oxygen through the protective film of oxide and the application of the diffusion laws to this process lead us to expect that the oxidation law will be

$$W^2 = Kt$$

W^2 = amount of oxygen absorbed
t = time
K is a constant

Pilling and Bedworth showed that the metals copper, nickel, zinc and iron obey the parabolic law with considerable accuracy at elevated temperatures At lower temperatures they found that the behaviour of copper is abnormal, the oxidation varying apparently capriciously They attributed these irregularities to the cracking of the oxide film and arrived at a limiting value for the oxidation rate of copper by drawing a curve through their lowest values This procedure is perhaps open to criticism.

Cadmium and aluminium were found to conform to the parabolic law for a while after which the oxide apparently became impervious and the attack of oxygen fell below measureable limits Pilling and Bedworth advanced no explanation, but the suggestion of U R. Evans, that a change in the properties of the oxide had occurred by sintering or recrystallisation, affords a satisfactory explanation of this behaviour For oxides of such high melting points as alumina and cadmium oxide the sintering will be extremely slow at temperatures of 600° C and 300° C respectively, and this will account for the extremely long period of conformity observed

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* ' J Inst. Met ,' vol. 29, p. 529 (1923)

The experiments of the present author on the low temperature oxidation of copper afford some support for this view

It is therefore to be expected that accurate conformity to the parabolic oxidation law will only be observed under conditions which lead to the formation of an oxide film whose properties remain constant in time During the course of an investigation of the oxidation of the copper zinc alloys the details of which it is hoped to publish later it became necessary to review critically the conclusions of Pilling and Bedworth and to formulate a more fundamental theory of oxidation and diffusion

Data for the oxidation of alloys of the following compositions are available for publication

—	No 3	No 8	No 9
Copper	7 86	90 37	95 10
Lead	02	< 0 01	< 0 01
Iron	0 04	0 03	0 04
Aluminium		0 005	0 004
Arsenic		< 0 005	< 0 005
Zinc by difference	29 08	9 58	4 84

The oxide from No 3 consists of almost pure zinc oxide although at the lowest temperatures the copper content may rise to 11 5 per cent

The oxides from No 8 and No 9 consist of cuprous oxide and zinc oxide apparently in solid solution with the copper zinc ratio essentially identical with that prevailing in the alloy *i e* 90 per cent and 95 per cent copper respectively

The experimental methods of Pilling and Bedworth were followed closely in one series of experiments Oxygen was passed over the specimen under examination which was heated in an electric furnace and the extent of oxidation was established by weighing the specimen after treatment for five hours

In a second series of experiments designed specially to study the form of the oxygen absorption/time curve the specimen was enclosed in a silica tube with pure dry oxygen and observations were taken of the volume decrease at constant pressure It was found that the two alloys containing 95 and 90 1 per cent of copper follow the parabolic curve

$$W^2 = Kt$$

with accuracy The alloy containing 70 per cent of copper follows a law of the same type

$$W^n = Kt$$

but n is rather higher than 2

The behaviour of these alloys is summarized in the following tables —

The oxidation of Brass containing 95 per cent Cu

Temperature	Wt of O_2 absorbed in mgms. per sq cm in 5 hours	Oxidation constant grs ^{2}/cm ^{4} per hour
650	2 83	1 60 $\times 10^{-6}$
725	6 32	8 00 $\times 10^{-6}$
800	12 0	2 88 $\times 10^{-5}$
880	21 2	9 0 $\times 10^{-5}$
	21 4	9 2 $\times 10^{-5}$

The oxidation of Brass containing 90 per cent Cu

Temperature	Wt of O_2 absorbed in mgms. per sq cm in 5 hours	Oxidation constant grs ^{2}/cm ^{4} per hour
580	0 615	7 59 $\times 10^{-8}$
650	1 83	6 7 $\times 10^{-7}$
725	4 62	4 28 $\times 10^{-6}$
800	9 20	1 69 $\times 10^{-5}$
880	1 83	6 70 $\times 10^{-5}$

Oxidation of Brass containing 71 per cent Cu

Temperature	O_2 absorbed in mg per sq cm in 5 hours	Oxidation rate "constant * grs ^{2}/cm ^{4} per hour
580°	0 21 0 183 0 187 0 144	8 82 $\times 10^{-9}$ 6 70 7 00 4 15
650°	0 41 0 367	3 36 $\times 10^{-8}$ 2 70
725°	0 875 0 810 0 823	1 54 $\times 10^{-7}$ 1 32 1 36
800°	1 62 1 80	5 25 $\times 10^{-7}$ 6 49
880°	3 36 3 90 3 52	2 26 $\times 10^{-6}$ 3 04 2 58

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* This value is calculated from the extent of oxidation after 5 hour periods upon the assumption of conformity to the parabolic law in order to facilitate comparison with other results. The fact that this law is not accurately obeyed in no way invalidates the conclusions of this paper The adoption of a more complex empirical oxidation law would mean an alteration in the slope of the $(\log K) \Big/ \frac{1}{T}$ curve without any change in the nature of the curve itself

The expression of Pilling and Bedworth connecting temperature and oxidation rate

$$K = aT^{\theta}$$

K = oxidation rate constant
T = temperature,
a and θ are constants,

was found to hold for these alloys, but since it is impossible to attach any physical meaning to an equation of such a type, this expression has been discarded. If, however, logarithms of reaction velocity constants are plotted against the reciprocals of absolute temperatures, excellent straight lines are obtained. Fig. 1 embodies the results of this investigation and also Pilling and Bedworth's observations upon copper, iron and nickel. Copper appears to give two intersecting straight lines. This point will be discussed later.

This result which is shown graphically on p. 209 may be stated analytically

$$\frac{d \log_e W}{dT} = \frac{-Q}{RT^2}$$

or

$$W = Ae^{-(Q/RT)}$$

where

W = oxidation rate
T = absolute temperature,
A and Q are constants.

The magnitude of the temperature effect immediately rules out any mechanism of oxidation founded upon the passage of oxygen through discrete cracks or channels. Such a mechanism would have a temperature coefficient of about 1·01 for 10° rise in temperature. The observed temperature coefficient of 1·3–1·5 is quite compatible with a process of actual solution of oxygen in the oxide.

It is necessary to devise a theory to account for a rapid exponential rise in the rate of diffusion of oxygen. There is no property of the oxide as a whole which can possibly account for such a rapid rise, and consequently we must look for some property of a few individual crystal units.

Let us make two assumptions both of reasonable probability. Firstly, that the structural units of the oxide are in a state of vibration and that a random distribution of energies of vibration prevails.

Secondly, that an oxygen molecule can only pass a structural unit provided that this possesses at the moment energy greater than a critical value causing a loosening of the oxide structure at that point.

If the distribution of energy in the solid is quantised the structural units may have energies

$$0,\ \mathrm{E},\ 2\mathrm{E},\ 3\mathrm{E} \quad n\mathrm{E}$$

The ratios of the probabilities of these events are

$$1 \qquad e^{-(\mathrm{E/RT})} \qquad e^{-(2\mathrm{E/RT})} \qquad e^{-(n\mathrm{E/RT})}$$

If in an aggregate of N units, M have zero energy

$$\mathrm{N} = \frac{\mathrm{M}}{1 - e^{-(\mathrm{E/RT})}}$$

Let the critical energy which a unit must possess in order to allow passage of oxygen be PE

The number having energy less than PE is

$$\mathrm{M}\,(1 + e^{-(\mathrm{E/KT})} \quad + e^{-(\mathrm{PE}-1)/\mathrm{RT}})$$

To obtain the number of units having energy greater than or equal to PE, we subtract the sum of this geometrical progression from the sum to infinity of the same series

Therefore number with energy PE or above is

$$-\,\mathrm{M}\,\frac{e^{\mathrm{PE/RT}}}{1 - e^{-(\mathrm{E/RT})}},$$

the ratio of these to the total number is

$$e^{-(\mathrm{PE/RT})}$$

The reaction constant K is proportional to this quantity

$$\mathrm{K} = k\ e^{-(\mathrm{PE/RT})}, \qquad \log_e \mathrm{K} = -\,\frac{\mathrm{PE}}{\mathrm{RT}} + \mathrm{const}\,,$$

$$\frac{d \log_e \mathrm{K}}{d\mathrm{T}} = -\,\frac{\mathrm{PE}}{\mathrm{RT}^2},$$

which is in formal agreement with the relationship found experimentally

It is difficult to state definitely what is the structural unit thus involved—the ion or the molecule—but this does not invalidate the general line of treatment outlined above The permeability of a solid is therefore linked with such properties as its vapour and dissociation pressures which are manifestations of a selected few specially active structural units—in this case one is tempted to say molecules

This theory is open to criticism, for the energy of activation Q which must be imparted in order to agitate the structural units sufficiently to allow the passage of oxygen or any other solute is given by the slope of the $\log_e K \Big/ \frac{1}{T}$ curve If this is large an oxide should be relatively impermeable, and the lower the rate of oxidation the greater should be the value of Q We find, however, that all the $\log_e K \Big/ \frac{1}{T}$ curves have approximately the same slope

It must be remembered, however, that oxidation rates are proportional to but not equal to the respective diffusion coefficients, and the extremely small value for the oxidation of aluminium is just as likely to be due to the extremely small solubility of oxygen as to a large energy of activation

The behaviour of copper is peculiar, for, as already noted, it apparently gives not one straight line but two when the log of its oxidation rate is plotted against the reciprocals of absolute temperatures It is difficult to say whether one is justified in resolving these data into two straight lines or whether the high temperature points lie on a curve continuous with the others It seems certain from Pilling and Bedworth's results that only at the highest temperatures is found a fully annealed film capable of plastic deformation, and it seems pertinent to enquire whether at the lower temperatures they are dealing with the same cuprous oxide as at the higher temperatures , whether in fact copper oxide produced below 600° C is not in a somewhat similar state to the oxides of aluminium and cadmium, and is much more permeable than a fully annealed specimen.

With alloys containing 90 per cent Cu, and 95 per cent Cu, a single straight line is observed down to temperatures of 580° C

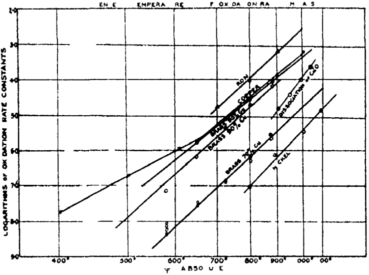
All the evidence seems to be in favour of attaching the greatest weight to the high temperature measurements and accepting the relationship

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

with its theoretical foundation as a true description of the variation of oxidation rate with temperature

The logarithms of the dissociation pressure of cupric oxide are plotted for comparison It will be seen that the slope of the dissociation pressure curve is considerably greater than that of the oxidation curve, so that we may conclude that the critical energy for formation of cupric oxide is greater than that necessary to allow the passage of oxygen by diffusion This would indicate that the intermediate formation of cupric oxide is not the mechanism of diffusion of oxygen through the layer of cuprous oxide

The equation which has been deduced for the influence of temperature upon diffusion rates should be valid also for other cases



Langmuir and Dushman* have shown that this relationship accurately describes the variation with temperature of the diffusion rates of gold in lead thorium in tungsten and sodium ions in glass

Summary

The oxidation of three copper zinc alloys has been investigated and shown to be controlled by diffusion through a protective film of oxide The rate of oxidation has been shown to vary exponentially with the temperature

A theory of diffusion in solid solutions has been outlined and by the application of statistical laws to the thermal agitation of solids an expression for the variation of diffusion rate with temperature has been deduced which is in formal agreement with the experimental law

The results of Robert Austen and Van Ostrand and Dewey upon the diffusion of gold in lead are shown to be in harmony with this hypothesis

The author wishes to thank Dr E K Rideal for much valuable advice and criticism and the Council of the British Non Ferrous Metals Research Association for permission to publish this work

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* Phys Rev vol 20 p. 113 (1922)

The Low Temperature Oxidation of Copper.

By J S DUNN, M.A , Ph D

(Communicated by Dr W Rosenhain, F R S —Received January 28, 1926)

The attack of dry air or oxygen upon copper becomes appreciable somewhere in the neighbourhood of 200° C The mechanism of the reaction in this temperature range has been studied by a number of authors but the absence of unanimity in their conclusions is remarkable It is evident that the oxidation of a metallic surface may result in the formation of a protective oxide film, and that continued oxidation may be controlled by the diffusion of oxygen through the film rather than by factors which are normally described as chemical Under these circumstances the progress of oxidation is precisely similar to the flow of heat and is subject to the same laws

If c is the concentration of oxygen at a distance y from the oxide—oxygen surface after a time t then

$$D \frac{\delta^2 c}{\delta y^2} = \frac{\delta c}{\delta t}$$

The solution of this equation is

$$C_x = C_0 \left\{1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} du\right\} \quad \text{where} \quad u = \frac{Y}{2\sqrt{Dt}}$$

If this expression is integrated with respect to C from $x = 0$ to $x = \infty$ we find that the total amount of oxygen passing across the surface is proportional to $\sqrt{t}$ or

$$W^2 = Kt \qquad \begin{aligned} W &= \text{oxygen absorbed as oxide} \\ t &= \text{time} \\ K &= \text{const.} \end{aligned}$$

is the ideal oxidation law. This is identical with the oxidation equation established experimentally for copper, nickel and iron at elevated temperatures by Pilling and Bedworth [*] They found that this law was obeyed above 600° C and with some reservations down to 300° C Tammann,[†] working at temperatures between 200° C and 300° C, made use of the phenomena of surface colours in order to follow the course of the reaction He assumed that the colours were due to the interference of light in the thin film of oxide From the colour of the film by normally reflected light, an estimate of the film thickness may be made,* but Tammann and Koster appear to have applied this principle incorrectly for they quote figures for interference by reflection from two surfaces, at only one of which a phase change occurs Actually, a phase change occurs both at the air-oxide interface and at the oxide-metal interface

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[*] 'J. Inst. Metals,' vol. 29, p. 529 (1923)

[†] 'Z Anorg Chem,' vol 123, p 196

Tammann's oxidation equation is

$$t = ae^{-bw} - a,$$

t is time, w amount of oxygen taken up and a and b are constants, the latter dependent upon temperature

W G Palmer† investigated a copper film rendered catalytically active by repeated oxidation and reduction, and concluded that in this special case the oxide formed had no protective effect and that the rate of oxidation was proportional to the square of the amount of unoxidised metal

Hinshelwood‡ recognised the protective action of the oxide but denied the interference theory of surface colours which forms the basis of Tammann's work

Hinshelwood's equation deduced in terms of pressure change measurements at constant volume

$$KA = \frac{1}{t}\left\{p_0 \log\frac{p_0}{p} - (p_0 - p)\right\}$$

showed upon experimental test variations of as much as 60 per cent in the constant KA

It seemed therefore highly desirable to discriminate between, or possibly to reconcile, the various conflicting views upon the oxidation of copper A few experiments were carried out by the surface colour method both upon commercially pure copper, cleaned by abrasion, and upon activated copper supported upon china clay rods The specimens were placed in an evacuated vessel which was surrounded by the vapour of a boiling organic liquid Air was allowed to enter upon the attainment of thermal equilibrium.

The application of the interference theory of the colours of surface films is beset by difficulties As a first approximation the colours may be assumed to be identical with the colours of Newton's rings by transmitted light, and an estimate of the film thickness may be made on this basis from Rollets table * This procedure involves the assumption that the phase changes at the air oxide and air metal interfaces exactly cancel each other and also ignores the effect of the dispersion of the film Other objections have been raised to the use of Rollets tables, based upon the fact that the conditions of transparency of the film and the reflectivity of the surfaces are not identical It is also essential that the composition and optical properties of the film shall remain constant during the time of the experiment

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* 'Z Anorg Chem.,' vol 111, p. 78, vol. 123, p 196

† 'Roy Soc Proc ' A, vol. 103, p. 444 (1923).

‡ 'Roy Soc. Proc, vol 102, p 318 (1922).

In expressing the thickness of the oxide film as estimated from the colour of the surface film relative values are used expressed as the equivalent air thickness This is the thickness of an air film which would produce the same colour and it will be shown later that in the case of coppper no serious error is involved in assuming that the thickness of the oxide film is proportional to the equivalent air thickness

In fig 1 a plot of the squares of thicknesses against time gives a series of

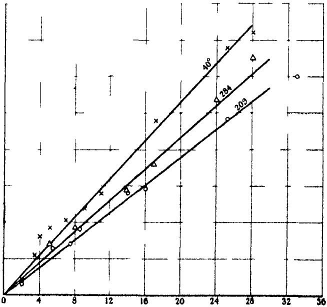

Fig 1 —The Oxidation of Commercial Copper
Abscissæ represent time in minutes for 240° and 209° in quarter minutes for 284°
Ordinates represent the square of equivalent thickness of oxide film

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* Wien. Ber vol 77 III, p 177

straight lines through the origin and confirms the relationship for the oxidation rate of normal or " commercial " copper,

$$y^2 = kt$$

The greatest reliance, however, cannot be placed upon the method for the reasons already outlined, and because it is necessary to draw sharp arbitrary distinction between tints which fade into one another continuously The experimental method of conductivity change developed by W G Palmer was accordingly adopted with some slight modification Palmer (*loc cit*) introduced his copper into a heated reaction tube which was filled with carbon dioxide He then exhausted before allowing the oxygen to enter This procedure is open to criticism for it is possible that oxidation, which is at first extremely rapid may take place to a certain extent before exhaustion is complete In the present investigation this possibility was eliminated by reduction *in situ*, and to this end an apparatus was constructed which is represented diagrammatically in fig 2

This consists of a tube closed with a ground glass stopper at S, which admits two leads of stout silver wire LL to the copper film R which is supported on a china clay rod A battery at B furnishes a current, the diminution of which measured in a calibrated milliammeter, M, enables rapid readings to be taken of the conductivity of the film Taps at P and A allow the exhaustion of the apparatus and the readmittance of air or hydrogen An organic liquid boiling in the glass outer tube Q furnishes a transparent vapour bath of constant temperature and enables observations of surface colour to be made simultaneously with those of conductivity

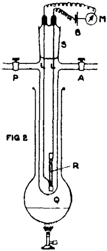

Fig 2

It was found that very reproducible results could be obtained with this apparatus, and that for a constant temperature of reduction, after one or two oxidations, the oxidation rate was independent of the previous oxidation history of the film

In order to ascertain the limitations of the method adopted in estimating film thickness from the surface colour, a specimen of activated copper was annealed for fifteen minutes at 444° C, and simultaneous observations of surface colour and resistance were made whilst the copper was undergoing oxidation

The observations are shown in fig 3, where the smooth curve drawn through the circles represents the fall in conductivity of the film Crosses represent the thickness of the film estimated by the surface colour method, from Rollets' table upon the assumption of an interference mechanism of the production of the colours The close correspondence of the thickness estimated by the two methods shows that no serious error is incurred in the case of copper by the neglect of the corrections and refinements already outlined Equally good correspondence between the two sets of figures has been obtained in every case tested The straight line in the figure is obtained by plotting squares of conductivity fall against time, and shows that the oxidation of the annealed film follows accurately the parabolic law over the time interval investigated

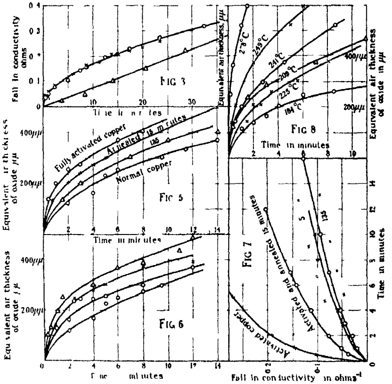

Fig 3 —Fall in Conductivity of Oxidised Copper

Figs. 5–8 —The Influence of Annealing (figs 5, 7), of Successive Reduction (fig 6), of Temperature (fig 8) on the Oxidation Rate of Activated Copper

A number of oxidations carried out upon activated copper at 209° C showed that the fall in conductivity was not strictly parabolic the later points on the curve showing a departure in the sense of a diminishing reaction velocity Aluminium cadmium and brass behave in a somewhat similar manner when undergoing oxidation at more elevated temperatures and the present author has attempted to account for this departure from the ideal oxidation law upon the basis of a change in the properties of the oxide film due to sintering or annealing which results in a lower permeability of the film to oxygen

The oxidation of copper afforded an excellent opportunity to test this hypothesis Oxidation was allowed to proceed to a stage characterised by the appearance of the first green surface colour and was then arrested by removal of oxygen by exhaustion The specimen was then kept at the temperature of oxidation for periods of 30 minutes and one hour respectively during which time annealing may take place Upon readmission of oxygen the reaction proceeded at a considerably reduced rate indicating with some certainty that a change in the properties of the film brought about by heat treatment had indeed occurred The results of typical experiments are shown in fig 4

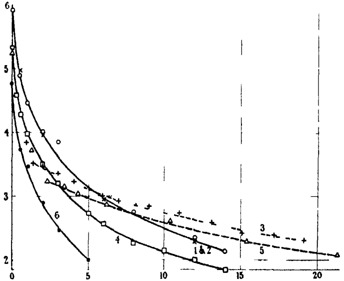

Fig 4 —The Oxidation of Activated Copper at 209° C

Abscissae represent time in minutes Ordinates represent conductivity of copper in reciprocal ohms.

Curves 1 and 2 are simple oxidations Curves 3 and 5 show the effect of arrested oxidation, and 4 is a check chronologically between 3 and 5 Curve 6 shows the effect of a series of oxidations at 306° upon the oxidation rate The constant difference in the ordinates of 1, 2, 4 and 6 illustrates the independence of oxidation rate upon previous oxidation treatment These curves are not coincident owing to a fall in conductivity of the copper film upon repeated reduction This is remarkable and seems to indicate a high volatility of the copper at the moment of reduction

If surface colour change be taken as the criterion the interesting fact emerges that activated copper oxidises considerably more rapidly than commercially pure electrolytic copper which has been cleaned by abrasion. It therefore seemed of interest to investigate to what extent circumstances which influence the catalytic activity of copper have a similar effect upon the oxidation rate

It has been shown* that a catalytically active copper is produced by the first reduction of cupric oxide This catalytic activity is raised very considerably by a second oxidation and reduction, but subsequent treatment has comparatively little influence The rate of oxidation is found to follow an exactly similar course

Annealing at temperatures above 400° C is known gradually to destroy catalytic activity, and accordingly copper films were annealed at the boiling point of sulphur, 444° C, for varying periods Films which had been thus treated oxidised according to the parabolic law, and the more slowly the longer their time of annealing These results are shown graphically in figs 5 and 6 in which the oxidation rates of variously treated copper films are compared by the surface colour method

In fig 7 the influence of annealing as judged by the conductivity measurements is shown The difference is much more pronounced than in the surface colour curves, and indicates that the annealing of an activated film is accompanied by two effects, a change in the nature of the surface which influences the thickness of oxide formed in a given time, and a change in the amount of surface exposed to oxidation which is revealed by the conductivity measurements.

The influence of temperature upon the oxidation rate of activated copper appears to be abnormal in the neighbourhood of 210° (fig 8) Copper oxidises apparently more slowly at 225° than at 209, and at 241° the oxidation rate is very little greater than at 209 Above 241° the variation with temperature once more becomes normal Palmer's explanation, that this abnormality is due to the fact that at about 200° cuprous oxide begins to compete with copper for the oxygen, is founded upon his theory of oxidation which is shown to be untenable A much more likely explanation is that cuprous oxide undergoes a transition in the neighbourhood of 200°–230° Indeed such a change has been shown to take place by the arrested oxidation experiments Whether this change is simply an annealing of a structureless oxide or a definite transition between two polymorphs, or possibly a combination of both effects, is a question to which no definite answer can yet be given

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* Constable, 'Roy Soc Proc.,' A, vol 107, p. 271 (1925).

The results of this investigation confirm in every way the hypothesis that the oxidation of solid copper is under all circumstances controlled entirely by the properties of a protective oxide film Any departures from this law may be accounted for by a variation in the properties of the film This affords some support for the theory advanced to account for the departure of certain metals from the parabolic oxidation law Palmer in his work on the oxidation of copper neglected the earliest points on his curves, and plotting the resistance of his film against time obtained a straight line He justified this procedure by postulating an adsorbed film of carbon monoxide which catalysed the earliest stages of oxidation and made the earliest observations unreliable

In the present investigation every effort was made to remove all trace of reducing gas with a Topler pump In the case of the annealed copper films this process was continued for as long as two hours at a temperature of 444° C, but nevertheless the relationship

$$\frac{dR}{dT} = K \text{ was never obeyed}$$

It is true that a close approximation to a straight line is obtained, but the curvature, especially among the earlier points, is definite and unmistakable

Tammann's logarithmic expression* for the oxidation of copper, founded as it is upon a fallacious application of interference principles, merits little serious attention

The parabolic relationship

$$W^2 = Kt$$

is therefore established for low temperatures as the ideal oxidation curve for copper, modified over long time intervals by a change in the state of the oxide

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* The present author has, however, confirmed Tammann's equation for the oxidation of iron in the neighbourhood of 300° C.

This result is in harmony with that established at higher temperatures by independent methods for copper and other metals.

The fact that an activated copper film oxidises considerably more rapidly than either an annealed or a cold worked specimen is of considerable importance

It is generally recognised that in the earliest stages, the orientation of the crystal units of an oxide film conforms to that of the underlying metal The structure of a metal may be brought out owing to the variation of the oxidation rate of different crystal faces. For a definite time of oxidation each crystal face will be characterised by a distinctive surface colour.

We are led to the conclusion that an abnormally permeable oxide film must reflect to some extent the structure of the underlying metal When copper is produced from cuprous oxide at low temperatures the spacing of the copper atoms in cuprous oxide will prevail at the moment of oxidation This distribution will be only momentary, for the action of interatomic forces will immediately come into play and will aggregate the copper into small crystal units. This process cannot proceed indefinitely for a contraction occurs, and the concentration of the copper on various nuclei will remove the outer atoms of the small crystal units beyond the interatomic distance from their neighbours We shall therefore have produced what is virtually a colloidal aggregate of copper atoms Whether the structure of cuprous oxide itself is preserved in the shape of small pseudomorphic units of copper is a question which could only be revealed by an X-ray spectrograph of extremely high dispersion Either a colloidal structure in which the number of atoms in the intercrystalline boundaries is comparable with the total number of atoms, or a structure in which an expanded or pseudomorphic copper lattice retaining to some extent the spacing of copper in cuprous oxide, will account for the increased oxidation rate

The X-ray examination of activated copper is in hand at the present moment at Manchester An examination of activated nickel in Prof. Bragg's laboratory* has revealed a broadening of the spectral lines, indicating in the opinion of the investigator that the nickel atoms occupy their normal lattice but that the crystals are of colloidal dimensions

Summary

The oxidation of copper in its normal commercial state has been shown to follow the theoretical parabolic law over comparatively short time intervals.

The oxidation of catalytically active copper has been shown to proceed more rapidly than normal copper, but the parabolic law is not obeyed

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* Private communication to Dr E. K. Rideal.

The origin of this departure from the ideal law has been traced to changes occurring in the oxide film and a general parallel has been established between catalytic behaviour and oxidation rate

The experiments described are considered to throw light upon the nature of catalytically active copper to which a disperse structure has been ascribed

I should like to thank Dr E K Rideal and Mr U R Evans for much valuable advice and criticism, and the Council of the British Non-Ferrous Metals Research Association for permission to publish this work

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The Effect of Temperature on the Viscosity of Air

By A O Rankine, D Sc, Professor of Physics in the Imperial College of Science and Technology

(Communicated by Prof H L Callendar, F R S —Received 4th February, 1926)

The recent measurements of F A Williams* of the viscosity of air from 15° C to 1002° C have produced unexpected results The greater part of this extensive temperature range has hitherto been quite inadequately investigated, and the new data, if correct, will obviously be of great value in relation to the theories of gaseous viscosity as a means of comparing their validities It is proposed to extend the measurements by the same experimental method to argon, which, being monatomic, is of special importance theoretically For these reasons it is essential that the accuracy of Williams's data should be satisfactorily established before acceptance An examination of these data in comparison with data from other sources in respect of the lower part of the temperature range reveals differences which cast doubt upon the reliability of Williams's values, and there are, besides, some features of his experimental work which are open to serious criticism.

Of previous investigations, that of Breitenbach† covers the largest temperature range—namely, from − 21 4° C to 302° C For purposes of comparison with Williams's results given in Table V of his paper,‡ Breitenbach's values, interpolated where necessary, are included in Table I, the last column of which gives the differences, expressed as percentages of Breitenbach's values

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* 'Roy Soc. Proc,' A, vol. 110, p 141 (1926)

† 'Ann d Phys,' vol 67, p 803 (1899)

‡ *Loc cit*, p 161

Table I

Temperature	Viscosity in C G S Units × 10^4		Difference per cent.
	Breitenbach	Williams	
°C			
0	1 733	1 719	0 8
50	1 976	1 926	2 5
100	2 207	2 124	3 8
150	2 430	2 319	4 6
200	2 625	2 512	4 4
250	2 810	2 704	3 8
300	2 985	2 886	3 3

It will be seen that whereas the results agree fairly well at 0° C, the difference of 0 8 per cent in the absolute values being probably due to errors in calibration, they separate rapidly from one another as the temperature increases The maximum difference occurs, curiously enough, in the neighbourhood of 189° C ; the lowest temperature, apart from the calibration of the capillary at atmospheric temperatures in terms of Millikan's viscosity data, at which Williams has recorded observations

The test of the relative reliability of Breitenbach's and Williams's data in the common region must depend to some extent on the support they have from yet other sources These are not numerous, but the viscosity of air in the neighbourhood of 100° C has been fairly frequently determined Landolt and Börnstein's Tables record several values, all close to $2\ 21 \times 10^{-4}$ C G S units, which distinctly favour Breitenbach's accuracy The comparison of the absolute values obtained by various observers is, however, open to obvious objections, it is fortunate, therefore, that we are able to apply a more stringent test All differences arising from errors of measurement of the dimensions or calibration of the capillary tube can be eliminated by dealing with the results of various observers expressed as *ratios* of viscosities at different temperatures Such ratios are measurable with much greater accuracy than is possible with absolute values Applying this method to Breitenbach's data at 100° C and 15° C, we obtain

$$\frac{\eta_{100}}{\eta_{15}} = \frac{2{\cdot}207}{1\ 807} = 1\ 221$$

Data are also available at 183° C for calculating the similar ratio $\frac{\eta_{183}}{\eta_{15}}$, for which Breitenbach's results give the value 1·419

We may treat the results of various recent observers in the same way introducing where necessary small temperature corrections to make the ratios strictly comparable Table II includes the work of Breitenbach and all subsequent observers recorded in the 1923 edition of Landolt and Börnstein s Tables

Table II —Values of the ratios $\frac{\eta_{100}}{\eta_{15}}$ and $\frac{\eta_{183}}{\eta_{15}}$ obtained by various observers

Observer	Reference	$\frac{\eta_{100}}{\eta_{15}}$	$\frac{\eta_{183}}{\eta_{15}}$
Breitenbach	Ann d Phys vol 67 p 803 (1899)	1 221	1 419
Schultze	Ann d Phys vol 5 p 140 (1901)	1 220	1 420
Tänzler	Verh d Phys Ges vol 8 p 222 (1906)	1 221	1 419
Pedersen	Phys Rev vol 25 p 225 (1907)	1 204	
Schierloh	Diss Halle (1908)	1 222	
Schmitt	Ann d Phys vol 30 p 393 (1909)		1 423
Rankine	Phys Zeit vol 11 p 745 (1910)	1 217	
	Mean values	1 218	1 420
Williams	Roy Soc Proc A vol 110 p 141 (1926)	1 190	1 370

It will be seen that whereas the results of previous observers for these viscosity ratios are remarkably consistent Williams s values are much lower than the means thus well established namely 2 5 per cent for the ratio $\frac{\eta_{100}}{\eta_{15}}$ and 3 5 per cent for the ratio $\frac{\eta_{183}}{\eta_{15}}$ Breitenbach s ratios on the other hand differ from the means by only one or two parts in a thousand The weight of evidence thus points to the probability of Williams s results being *relatively to one another* in error to the extent mentioned and to their being less reliable than Breitenbach s in the temperature region common to both Further it is not likely that under the more difficult conditions of measurement at the higher temperatures the accuracy would be improved

If we have to admit a possible error of 3 per cent in Williams s relative measurements the greater part of the significance of his curve in Fig 3* disappears The linearity of AB would not be so well established and its slope upon which the deduced value of Sutherland s constant *C* depends would become less determinate The magnitude of *C* is in fact so sensitive to variations in the slope of AB that apart from the present criticism the value given namely 172 6 to four significant figures is certainly not justified and errors of the order indicated would be capable of accounting for the difference between this surprisingly high value and that hitherto accepted—120 or thereabouts On the basis of the validity of this criticism, therefore, it is impossible to accept as satisfactory Williams's conclusion that Sutherland's law breaks down definitely for air at the relatively high temperature of 250° C., and its implication that all previous observations which have confirmed the law below this temperature are seriously in error That the law fails eventually is admitted, also that Sutherland's constant diminishes, but at low temperatures much nearer the critical temperature It may be remarked, moreover, that the value of approximately 70 for C, which Williams's own data give for the region between 0° C and 100° C, is quite inconsistent with Vogel's larger values, which are quoted,* for still lower temperature ranges

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* *Loc cit* p 162

The most probable source of error in Williams's experiments would appear to be the measurement of the high temperatures used On this question very little is said in his paper For each experiment a single temperature is recorded to an accuracy of 1 degree, and there is no mention of the fluctuations of the thermocouple indications over periods sometimes extending to more than two hours Moreover, although nothing is mentioned of a temperature survey of that part of the electric furnace occupied by the capillary tubes, a single thermo element near the entrance to the capillary appears to have been relied upon to measure the average temperature of the air in the capillary throughout its transpiration Having regard to the fact that the thermo-element was at the centre of the cylindrical tube of the furnace, while the greater part of the capillary spiral was near its inner surface and quite close to the actual heating coil, one would expect, without evidence to the contrary, that the capillary and the air in it would be hotter than the thermo-element, and that this discrepancy would increase at higher temperatures Such an under-estimation of the temperature would, at any rate, account for the rapid increase of viscosity apparently observed, and possibly provide an explanation of the differences to which attention has here been drawn

With reference to constancy of experimental conditions, it may be remarked also that the pressure differences recorded, although given to the high degree of accuracy corresponding to about 0 1 mm of the gauge fluid, give no indication of the behaviour of the manometer during observations, even though the pressure differences had to be maintained as nearly as possible constant by the operation of a valve by hand Absolute constancy under such conditions is evidently impracticable

Finally, reference should be made to a rather disturbing statement on page 152 of Williams's paper "The first capillary tested did not give concordant results and was rejected A second and more uniform capillary yielded the values given in Table I" No precise indication is given of the uniformity of either, so that the effect of non-uniformity on reliability of results cannot be estimated It is clear that large variations from cylindrical shape of the capillary are not permissible even for comparative purposes The only safe procedure, when some non-uniformity is inevitable owing to difficulties of manufacture at present associated with working quartz, is to ascertain whether Meyer's formula is valid for variations of the pressure difference

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* *Loc cit.*, p 163.

This test Williams does not appear to have carried out, his measurements, both in calibration and in the subsequent high-temperature work, being confined to pressure differences within 1 per cent of 73,200 "dynes" (presumably dynes/cm ^{2} is meant) Unless, at a given temperature, the transpiration times are related to the pressures in accordance with the formula assumed, the true viscosity is not being measured

It is suggested that Williams's experimental tube should be subjected to this test, and that the temperature survey of the furnace already mentioned should be carried out In this way his laborious and meritorious work already done and in contemplation would assume a greater value

Some Thermal Constants of Solid and Liquid Carbon Dioxide

By O MAASS and W H BARNES, McGill University, Montreal

(Communicated by Prof H T Barnes, F R S —Received February 13, 1926)

I —Introduction

Carbon dioxide is a substance whose properties have been the subject of innumerable investigations Particularly the pressure volume-temperature relationships when in the gaseous and liquid phases have provided data for the basis of equations of state The thermal properties are not so well known and an investigation of these is the purpose of the following paper

The actual measurements to be described deal with the direct determination of the latent heat of fusion, the latent heat of sublimation and the specific heats of the solid and liquid over the temperature range of 0° C to −184° C The experimental methods employed are of sufficient interest to warrant a detailed description Since it was found that the specific heat of the solid carbon dioxide gave abnormally high results the expansion coefficient of the solid was measured

Carbon dioxide is one of a few substances that develop a large vapour pressure in the solid state The specific heat and thermal expansion coefficient values are of interest in this connection Furthermore with a possible use of carbon dioxide as a refrigerant on a commercial scale the exact determination of the thermal properties of carbon dioxide is of practical importance

II —*Specific Heats and Latent Heat of Fusion*

(*a*) *Method* —The method employed in the determination of the specific heats and latent heat of fusion resembles that used by one of us for ice, benzene and other substances and was briefly as follows *

A closed metal container, filled with carbon dioxide, was weighed and then allowed to come to an initial temperature in a brass tube, so arranged that uniformity of temperature was established rapidly The container and contents were then removed to an adiabatic calorimeter where the heat taken up by the carbon dioxide and its container was measured, this being corrected to a final temperature of +25° C (*see* calculations) The container was next emptied and weighed, after which a blank test was made on the container alone over the same temperature range

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* Maass and Waldbauer, 'J A.C.S.,' vol. 47, p 1 (1925).

From these values the total heat per gram of carbon dioxide from a known initial temperature to +25° C. was calculated. A number of determinations were made with different initial temperatures and the total heats obtained were plotted on a curve. From this curve the latent heat of fusion of carbon dioxide was found and the specific heats calculated.

(*b*) *Apparatus*.—The adiabatic calorimeter that was used is shown in fig. 1. The copper calorimeter vessel (D) had a capacity of 1300 c.c., while the outer bath (K) contained 10 litres of water. The copper calorimeter was set on legs (G) that were cemented to the outer bath as shown. Considerable attention was paid to the stirring because of the necessity for a rapid equalization of temperature throughout the bath when hot or cold water was added. Four

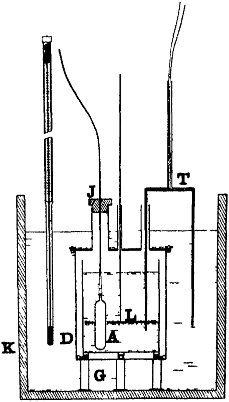

FIG. 1.

stirrers (not shown in figure), each with two pairs of propeller blades, were rotated in different directions so that each stirrer forced the water in the opposite direction to the one on each side of it. A multiple thermocouple (T) of copper and constantan was placed in the bath and calorimeter as shown and was used throughout the experiments as a null instrument

By the addition of hot or cold water the outer bath was always kept at the same temperature as the inner calorimeter water to within 0 0005° C Even when large temperature changes were taking place in the calorimeter, as when the cold container was suddenly introduced, it was possible to keep the temperature difference to within 0 01° C The temperature of the outer bath, which was the same as that of the inner calorimeter, was measured by means of a Beckmann thermometer Readings were taken to 0 001° C This thermometer had been calibrated by the Bureau of Standards and all the precautions necessary for its use as a precision instrument were taken

The stirring in the calorimeter was accomplished by the up and down motion of a copper disc (L), appropriately perforated to permit the free passage of the thermocouple and the carbon dioxide container The weight of the disc was sufficient to permit rapid stirring, which was regulated by an electrically driven, adjustable eccentric The calorimeter vessel was insulated from its jacket by three small ivory knobs affixed to pegs at the bottom The cover of the jacket was tightly clamped to a ledge at the top, which was well greased with vaseline This made a very effective water-tight joint A tube, wider than the carbon dioxide container, was soldered into the centre of the cover to permit the entrance of the container to the calorimeter proper Three other tubes of appropriate diameters served for the thermocouple arm and for the two stirrer wires.

The following constant temperature baths were used to enable the carbon dioxide to be brought to a known initial temperature before placing in the calorimeter

An ice-water mixture gave the 0° C bath Solid carbon dioxide moistened with ether was used for −78 5° C Liquid air, obtained from an air liquefaction plant and therefore practically pure oxygen, gave the lowest constant temperature bath employed. In the latter case analysis of the liquid air for oxygen content was resorted to in order to obtain the exact temperature.*

For temperatures between 0° C and −78 5° C a large Dewar flask filled with ether and vigorously stirred by a current of dried air was used The ether was brought down to the required temperature by the rapid addition of solid carbon dioxide and could then be maintained at the desired temperature to within 0 1° C by the addition of small lumps of carbon dioxide A somewhat similar arrangement was employed to obtain a constant temperature bath for any point between −78 5° C and liquid air temperature The ether was replaced by the first distillate from petrolic ether which remains fluid to very low temperatures Liquid air was forced into a glass cooling bulb (*see* fig 2) rapidly at first and then as required to maintain a constant temperature Stirring was effected as before by bubbling dry air from E through the petrolic there a constancy of 0 1° being readily obtained

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* George Claude, 'Liquid Air, Oxygen, Nitrogen,' p. 231 (1913).

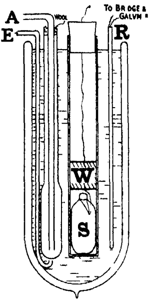

FIG 2

The temperatures of the baths were read by means of a platinum resistance thermometer with compensating leads of the Callendar Barnes type which was operated through a resistance box a variable mercury resistance and the galvanometer used in the thermocouple circuit

(c) *Procedure*—The container for the carbon dioxide was made of iron had a capacity of 10 c c and contained about 8 grams of carbon dioxide It was metal sealed and was strong enough to withstand the pressure due to liquid carbon dioxide up to room temperature The container was weighed before and after each run to make certain that no loss of carbon dioxide occurred due to leakage

This weighed container (see S in fig 2) filled with carbon dioxide was placed in a brass tube of such a diameter that the container could just pass easily through it One end of the tube was closed water tight while the other was stopped with a cork to which the container was attached by means of linen thread Two copper discs enclosing wool (see W in fig 2) served to insulate the container from the upper part of the tube Electric tape was wound over the side of the cork and the top of the tube This prevented any moisture condensing on the cork or the tube and eliminated the danger of introducing water from this source into the calorimeter

The brass tube was then suspended in the constant temperature bath and allowed to remain at a known initial temperature for a sufficient length of time to permit the carbon dioxide and container to come to this temperature From 1 to 1½ hours was found to be quite satisfactory For the points below −60° C. the brass tube and contents were kept in solid carbon dioxide moistened with ether for 1 hour before placing in the constant temperature bath This was done to prevent supercooling of the carbon dioxide It will be seen in the curve obtained for the heat content of carbon dioxide (see fig. 3) that one determination at −61 4° C did supercool This happened before the necessity for precooling the carbon dioxide well below its melting point was recognized

While the carbon dioxide was in the constant temperature bath the adiabatic

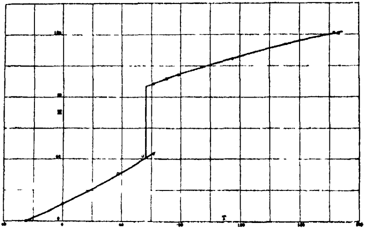

Fig 3.

calorimeter was prepared as follows The inner calorimeter vessel was weighed empty and dry It was filled with water at a suitable temperature and reweighed. After placing in the calorimeter jacket the cover was immediately clamped into place, the tubes in the cover for the introduction of the thermocouple and the container being stopped with corks. The calorimeter bath was immediately filled with water to the overflow, which allowed water to completely surround the calorimeter jacket, including the cover. The thermocouple was set in place with one arm in the calorimeter and the other in the water of the outer bath. By running in hot or cold water the temperature of the water in the outer bath was brought slightly higher than that in the calorimeter proper and maintained at this higher value until the calorimeter was required for use The reason for maintaining this slight difference in temperature was to prevent any distillation of the water from the calorimeter to the top and walls of the calorimeter jacket

Shortly before the time for the introduction into the calorimeter of the carbon dioxide and container the water in the outer bath was brought to exactly the same temperature as the water in the calorimeter proper From this point to the end of the experiment the two baths were kept as nearly as possible at the same temperature

The Beckmann thermometer was read every five minutes until three successive readings did not vary more than 0 002° from one another Conditions in the calorimeter were then known to be constant

The electric tape was removed from the brass tube in the constant temperature bath and the carbon dioxide in its container was rapidly transferred to the calorimeter (see A in fig 1), the cork to which the container was affixed fitting the tube through which the container was introduced into the calorimeter (see J in fig 1) Appreciable heat loss in the transference of the carbon dioxide to the calorimeter was avoided since the time required to remove the container from the constant temperature bath to the calorimeter was less than three seconds The insulating plug of wool and copper discs automatically fell off as the container was removed from the brass tube

Cold water was rapidly run into the water-bath surrounding the calorimeter as the water in the calorimeter cooled down When a constant temperature had again been reached, readings of the Beckmann thermometer were taken every five minutes until three successive readings agreed with one another to 0 002°

(*d*) *Sample Set of Observations*—The following set of observations are characteristic of those obtained throughout —

Initial temperature = − 78 5° C

Weight of calorimeter and water = 925 00 gms

Weight of calorimeter = 269 45 gms

Weight of water = 655 55 gms

Weight of calorimeter, stirrer and thermocouple arm = 298 2 gms

Specific heat of calorimeter, stirrer and thermocouple arm = 0 0827 cals per gram

Beckmann thermometer readings.—

Time.	Beckmann.
9·00 p.m.	3·543
0·05 ,,	3·543
0·10 ,,	3·542
0·15 ,,	3·543

Introduced carbon dioxide and container —

Time	Beckmann
9·20 p.m.	2·100
0·25 ,,	2·100
0·30 ,,	2·101

Weight of container and carbon dioxide = 29·5092 gms

Weight of container = 21·4800 gms

Weight of carbon dioxide = 8·0292 gms

(*e*) *Calculations and Results*.—The following set of sample calculations are based on the observations given above

Calorimeter temperature —

Initial	−3·543	Final	−2·100
Correction for standard	0·0001		0·0030

Temperature change of calorimeter . = 1·4459° C

Setting factor for Beckmann thermometer = 1·000

Weight of water = 655·55 gms

Heat given up by calorimeter, stirrer and thermocouple arm

= 298·2×0·0827×1·4459

= 35·658 calories.

Heat given up by water

= 655·55×1·4459

= 947·863 calories

Total calorimeter heat change

= 983·52 calories

Heat taken up by carbon dioxide and container near +25° C

= 6·6 cals per degree

(from preliminary curve of Total Heats) *

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* Since the end temperature was always less than 1° either above or below 25° C, a preliminary curve of Total Heat taken up by carbon dioxide and container was plotted against Initial Temperature (neglecting end temperature) and the slope was determined in the region of liquid carbon dioxide From this slope the number of calories taken up per degree was found and was used to correct the Total Heat taken up to an end temperature of 25° C

Final temperature of container and contents

= 2 10° (Beckmann)

= 23 65° C

Total heat taken up by carbon dioxide and container from

−78·5° C to +25° C = 992 43 calories

The calculation is self explanatory and it will be seen from it how the heat change is always calculated to the same end temperature

The values for the total heat change, given in Table I, are the means of several determinations that agreed with one another to within 0 5 per cent

Table I

Initial Temperature of Carbon Dioxide and Container	Total Heat (Calories) taken up by Carbon Dioxide and Container from Initial Temperature to +25° C
+25 0° C	0 0
0 0° C	151 9
−37 5° C	396 5
−54 3° C	509 5
−61 4° C (Super cooled)	547 8
61 4° C (Solid)	908 3
−70 6° C	951 4
−78 5° C	990 3

The values given in Table I were plotted on a curve* from which the rise in the heat taken up by the carbon dioxide at −56 2° C (the melting point) was equal to 364 calories

Hence the latent heat of fusion is equal to this rise in the heat taken up divided by the weight of carbon dioxide in the container.

Latent heat of fusion of carbon dioxide

$$= \frac{364}{8\ 029}$$

= 45 3 calories per gram

as compared with the value 43 8 found by Kuenen and Robson †

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* This curve is not given here but was similar to fig. 3, except that Total Heat of container and contents was plotted against Initial Temperature on a large scale

† 'Phil Mag,' vol. 3, p. 622 (1902)

To obtain the specific heats of the solid and liquid carbon dioxide the specific heat of the container* was determined over the temperature range −183·1° C. to +25° C and a number of additional determinations of the total heats of the carbon dioxide and container were made

The heat content per gram of container and the heat content per gram of carbon dioxide are given in Table II below

Table II.

Temperature	Heat Content per Gram (Calories)	
	Container	Carbon Dioxide
+25 0° C	0 00	0 00
0 0° C	2 95	11 04
−37 5° C	7 00	30 58
−54 3° C	8 20	41 90
−61 4° C (Super-cooled)	9 20	43 38
−61 4° C (Solid)	9 20	88 47
70 6° C	10 02	91 70
−78 5° C	10 78	94 34
115 0° C	13 30	104 7
183 1° C	17 80	120 9

In Table II, column 1 gives the initial temperature of container and contents, columns 2 and 3 the heat required to warm up one gram of container and one gram of carbon dioxide respectively from the initial temperature to +25° C. Thus, for example, the third to last figure in column 3 (namely 94 34) means that it requires 94 34 calories to warm up one gram of carbon dioxide from −78 5° C (its boiling point) to +25° C, without evaporation

The values for the heat content per gram of carbon dioxide given in Table II are plotted against temperature in fig 3, where H represents heat content per gram of carbon dioxide and T represents temperature in degrees centigrade.

In Table III below are given the average specific heats of carbon dioxide over several temperature ranges.

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* It is of interest to note that the average specific heat of iron over the range −183 1° C. to +25° C was found to be 0·0855 in agreement with the value found by Richards and Jackson over the same temperature range (' Z phys. Chem.,' vol. 70, p. 414 (1910))

Table III

Temperature Range	Average Specific Heat
+25° C to −56 2° C	0 490 cals per gm per deg
−56 2° C to −78 5° C	0 348 cals per gm per deg
− 78 5° C to −115 0° C	0 284 cals per gm per deg
−115 0° C to −183 1° C	0 231 cals per gm per deg

By taking tangents to a curve of the total heats plotted to a large scale the specific heats of the solid carbon dioxide (C_p) could be represented over the temperature range (−56° C to −110° C) by the equation

$$C_p = 0\ 400 - 0\ 00283\ T + 0\ 0000125\ T^2$$

where T represents temperature in degrees absolute

The values for the specific heat at various temperatures are given in Table VII Eucken* obtained 0 294 and 0 295 at 195 2° A and 196 4° A respectively as compared with 0 324 and 0 326 found by the authors

The results obtained for the molecular heats (at constant pressure) of solid carbon dioxide are of considerable interest The average value for the molecular heat over the temperature range from the boiling point (−78 5° C) to the melting point (−56 2° C) was found from the foregoing results to be 15 312, this value decreasing to 12 496 over the lower range of −115 0° C to −78 5° C Both these values are much larger than the molecular heat obtained for carbon dioxide in combination at much higher temperatures The average molecular heat of compounds such as RCO_3 is 20 7 and that of the oxides RO is 11 1 so that the average molecular heat of carbon dioxide in combination is 9 6 The molecular heats are of course all measured at constant pressure, and it is to be inferred from the above comparison that the molecules in pure solid carbon dioxide are not held together as firmly as the carbon dioxide when combined with metallic oxides

In corroboration of this fact it was noticed that solid carbon dioxide has a much greater thermal expansion coefficient near its melting point than is ordinarily attributed to a solid Measurements of this expansion coefficient have been made and will be described in detail later

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* 'Ber Deut physikal Ges.,' vol. 18, pp 4-17 (1916)

III.—Latent Heats of Sublimation and Evaporation

(*a*) *Method.*—In the determination of the latent heat of evaporation of carbon dioxide a special apparatus was designed by means of which pure carbon dioxide could be generated and a known weight then condensed into a container. The container and contents did not have to be weighed at room temperature so that there was no necessity of having a container that would withstand any appreciable pressure.

The solid carbon dioxide was allowed to warm up in an adiabatic calorimeter, and the heat taken up by it from a known initial to a known final temperature was accurately determined.

During this rise in temperature the container was open to the air so that the carbon dioxide evaporated, the final temperature of the gas formed being that of the calorimeter.

(*b*) *Apparatus.*—The apparatus for the generation and condensation of the carbon dioxide is shown in fig. 4.* Dilute sulphuric acid (1 : 6) was contained

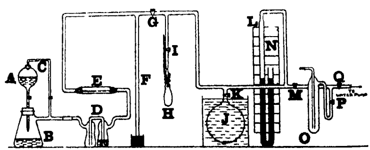

Fig. 4.

in the dropping funnel (A) and allowed to drop on a saturated solution of potassium carbonate in the flask (B). The carbon dioxide so produced was dried by passage through the concentrated sulphuric acid bubblers (D) and then over phosphorus pentoxide in the tube (E). By observation of the mercury manometer (F) the pressure of the carbon dioxide generated could be maintained at that of the atmosphere. The dried gas was collected in the volume bulb (J), the pressure in this part of the apparatus being determinable at all times by means of the mercury manometer (L).

Condensation was effected in the glass bulb (H). The first attempt was made with a metal container fitted with a metal spiral as a receptacle for the condensed carbon dioxide, but it was found to have too high a heat conductivity Even with the spiral surrounded by a steam coil it became so cold that carbon dioxide was condensed in it, thus blocking the passage to the container proper Consequently the metal container was replaced by the glass bulb which was found to be very satisfactory

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* The distillation flask and the (O) taps (P) and (Q) were sealed on for the determination of the coefficient of expansion to be described later.

The bulb (H) was constructed to have a volume of about 20 c c A glass tube at the top facilitated sealing to the main part of the carbon dioxide apparatus and could be sealed off completely after condensation of the carbon dioxide The bulb was also fitted with a thin-walled glass spiral of small bore through which the carbon dioxide was allowed to escape during the heat change measurements The object of the spiral was to ensure the escaping carbon dioxide being at the same temperature as the water in the calorimeter This spiral was a very important feature of the glass container The thickness of the walls was about 0 1 mm and the diameter of the tube was less than 2 mm Before placing in the calorimeter the tip of this thin tube was broken, and since the other tube from the bulb was sealed off, the carbon dioxide could only escape through the spiral. In this way all the escaping carbon dioxide was enabled to come to the temperature of the water before leaving its influence

The whole apparatus could be evacuated by means of a vacuum pump It was found advantageous only to evacuate that part of the apparatus to the right of tap (G), the left-hand section being maintained always at atmospheric pressure. This eliminated the danger of air leakage through the rubber connection between the flask (B) and the rest of the apparatus that might have taken place due to the higher pressure on the air side of the tubing A rubber connection was used in order that the generator might be easily removed and cleaned out when the solution of potassium carbonate was used up Except at (B) all connections were glass blown to prevent any leakage in the apparatus

(c) *Procedure*—The whole apparatus was swept out at least five times with carbon dioxide by evacuation of the part to the right of tap (G) followed by generation of carbon dioxide in the flask (B), which passed through the partially opened tap (G) After filling all the apparatus with carbon dioxide at atmospheric pressure, taps (G) and (M) were closed, care being taken to see that taps (I) and (K) were open

A piece of tissue paper was tied around the bulb (H) and a Dewar flask filled with liquid air was carefully brought up under it When using the bulb (H) without the tissue paper it was found that during the condensation of the carbon dioxide, even with dry air blowing around the condensation bulb, it was impossible to prevent the deposition of a certain amount of water on the surface of the bulb Consequently the values for the heat change when this took place were found to be a few calories too high and therefore were rejected. Results checking to better than 0 5 per cent were obtained by the use of the tissue paper This paper prevented the condensation of water on the bulb, and the time to remove it before placing the bulb in the calorimeter was negligible since it could be torn off at one stroke.

As condensation took place in the bulb (H) the left-hand column of the manometer (L) rose. Tap (I) was then closed and the positions of the mercury in the two arms of the manometer (L) were obtained from the scale (N). The apparatus was refilled with carbon dioxide at atmospheric pressure by partially opening tap (G) Tap (G) was then reclosed and, on opening tap (I), further condensation took place in the bulb (H) as shown by the rise in the left-hand column of the manometer (L) Tap (I) was closed again and the manometer read as before The apparatus was filled a third time with carbon dioxide at atmospheric pressure and condensation was effected as already described

Note was made at the time of barometric pressure, room temperature, and the temperature of the water-bath surrounding the volume bulb (J). The glass tube connecting bulb (H) to the apparatus was sealed off completely and the bulb was immersed in liquid air for 30 minutes

When the adiabatic calorimeter was ready the tip of the glass spiral of bulb (H) was broken, the tissue paper was torn off and the bulb was transferred rapidly to the calorimeter where the heat changes occurring were carefully noted.

It was very important to have the end of the glass spiral project above the cover of the calorimeter jacket when the bulb was in the calorimeter proper It was found that the total heat from −183·1° C to +25° C was 191·5 calories as compared with the probably correct value of 183 calories when the carbon dioxide was allowed to escape from the bulb (H) into the space between the calorimeter proper and the calorimeter jacket. This is explained by the fact that a certain amount of water probably evaporated into the dry carbon dioxide gas circulating above it Even the evaporation of a small amount of the calorimeter water would have an appreciable effect on the heat measurements because of the large latent heat of evaporation of water

In order to calculate the amount of carbon dioxide in the bulb (H) it was necessary to know accurately the different volumes present from which it was condensed. The volume of the bulb (J) was determined in the usual manner by filling with water and weighing. The volumes of the tubing and bulb (H) were determined by filling bulb (J) with air at atmospheric pressure, evacuating the tubing, opening taps (K) and (I) and reading the manometer pressure.

(*d*) *Calculations and Results*.—The mean of several determinations, agreeing with one another to better than 0·5 per cent., gave the total heat of carbon dioxide (solid and gas) from −183·1° C. to +24·6° C.

= 183·0 calories per gram.

From Table I the total heat of carbon dioxide (solid) from −183·1° C. to −78·5° C.

= 26·56 calories per gram.

Taking the mean specific heat of carbon dioxide gas from tables* as 0·19, then the total heat of carbon dioxide from 0° C. to +24·6° C.

= 4·67 calories per gram.

Hence the total heat of carbon dioxide from −78·5° C. to 0° C.

= 183·0 − 26·56 − 4·67

= 151·8 calories per gram.

Now the heat required to warm carbon dioxide gas from −78·5° C. to 0° C.

= 78·5 × 0·19

= 14·9 calories per gram.

Hence the latent heat of sublimation of carbon dioxide

= 151·8 − 14·9

= 136·9 calories per gram.

Andrews† has recently measured the latent heat of sublimation of carbon dioxide, obtaining the somewhat higher value of 151 calories per gram as the mean of a large number of determinations that do not agree nearly as well with one another as the various values obtained by the authors. The difficulty pointed out by Andrews of obtaining good thermal contact due to the high insulating property of the carbon dioxide snow itself falls away altogether in the method adopted in this laboratory.

From Table III the average specific heat of solid carbon dioxide from −78·5° C. to −56·2° C. is 0·348, so that the heat required to warm solid carbon dioxide from −78·5° C. to −56·2° C.

= 0·348 × 22·3

= 7·76 calories per gram.

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* Landolt-Börnstein, 'Phys. Chem. Tab.,' p. 1274 (1923).

† 'J.A.C.S.,' vol. 47, p. 1597 (1925).

And the heat required to warm carbon dioxide gas from $-78{\cdot}5°$ C. to $-56{\cdot}2°$ C.

$$= 0{\cdot}19 \times 22{\cdot}3$$

$$= 4{\cdot}24 \text{ calories per gram}$$

So that the latent heat of evaporation of carbon dioxide

$$= (136{\cdot}9 + 4{\cdot}24) - (45{\cdot}3 + 7{\cdot}76)$$

$$= 88{\cdot}1 \text{ calories per gram}$$

IV.—*Coefficient of Expansion*

(*a*) *Method*.—The general method employed in the determination of the coefficient of expansion of carbon dioxide was to condense a definite weight of carbon dioxide in a small glass bulb fitted with a graduated capillary tube. A known weight of gas was then condensed in the bulb as a liquid, completely filling the bulb and part of the capillary tube, which was then sealed off.

The position of the liquid in the capillary tube was read at different temperatures from the graduations on the glass. Then, knowing the weights of carbon dioxide and of liquid respectively, and the densities of the liquid at the various temperatures, it was possible to calculate the densities of the carbon dioxide at these temperatures. From the values so obtained the coefficient of expansion of solid carbon dioxide at various temperatures was calculated.

(*b*) *Apparatus*.—The apparatus for the condensation of the carbon dioxide and the liquid was the same as that used in the determination of the latent heats of sublimation and evaporation. A distilling flask (O) for the liquefied gas, together with taps (P) and (Q), was sealed to the apparatus between tap (M) and the vacuum pump. (See fig. 4.) The gas was kept liquefied by surrounding the distilling flask with liquid air.

The density bulb had a volume of about 3.5 c.c. and was glass sealed to the apparatus in the position occupied by the bulb (H) in fig. 4. The graduated capillary sealed to it was carefully calibrated.

Constant temperature baths similar to those previously described were used.

(*c*) *Procedure*.—Some preliminary tests were made on the solubility of carbon dioxide in petrolic ether (B.P. < 35° C.). The petrolic ether was cooled with solid carbon dioxide and was then drawn through a filter of linen and glass wool into lime water. There was no indication of the solubility of carbon dioxide. Petrolic ether was, however, abandoned as a liquid suitable for the measurements because of its variable composition and the experimental difficulty of adding definite quantities to the density bulb when filled with solid carbon dioxide

Since this ether consisted of a mixture of saturated hydrocarbons it was replaced by propane which could be prepared with great purity, could be handled in the gaseous state, and the density of which in the liquid condition had already been determined to a certain extent *

The propane was made by allowing normal propyl iodide to act on zinc-copper couple in the presence of alcohol The liberated gas was passed through concentrated sulphuric acid and then condensed by means of solid carbon dioxide moistened with ether The liquefied propane was then allowed to distil into a gasometer in which it was stored over water The propane so obtained was purified by passing three times successively through alcohol and over more zinc copper couple It was then passed through concentrated sulphuric acid to remove all moisture and was condensed by means of solid carbon dioxide moistened with ether After several distillations, when no residue remained in a flask on allowing it to warm up to 0° C, the propane was finally distilled into the flask (O) attached to the condensation apparatus (see fig 4) which was then sealed off from the air

Carbon dioxide was condensed into the density bulb by the same procedure as before The apparatus was then swept out with propane and the propane was finally allowed to condense in the density bulb in the same manner as the carbon dioxide, care being taken that the bulb was filled completely with the liquid The density bulb was then sealed off from the air

Readings of the capillary were taken in solid carbon dioxide moistened with ether, in liquid air, and at a number of temperatures between $-78\ 5°$ C and $-140°$ C For these latter determinations the petrolic ether constant temperature bath was employed

Since the density of liquid propane was only known to about $-78\ 5°$ C additional determinations were made using the method employed by Maass and Wright The density bulb for these experiments was fitted with a small bulb at the top so that the liquid propane could be warmed up to room temperature and then weighed Readings of the capillary were taken in liquid air and in the petrolic ether bath at different temperatures

Table IV below gives the densities of propane as found They agree with those obtained by Maass and Wright at higher temperatures

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* Maass and Wright, 'J A C S.,' vol 43, p. 5 (1921)

Table IV.

Temperature (° C)	Density
−183·3	0·7390
−139·0	0·6895
−133·3	0·6841

The density determinations of the carbon dioxide were repeated using a larger amount of carbon dioxide in the density bulb and also a new sample of propane, prepared and purified in the same manner as the first amount.

(*d*) *Calculations and Results*.—The following calculation is typical of those made throughout this determination :—

Weight of propane = 0·4767 gms

Weight of carbon dioxide = 4·8939 gms

Temperature = −115·2° C

Volume of density bulb to point of meniscus corrected for temperature = 3·7581 c.c.

Density of propane (from curve) = 0·6642

Volume occupied by propane $= \dfrac{\text{Weight}}{\text{Density}}$

$= \dfrac{0·4767}{0·6642}$

= 0·7177 c.c.

Volume occupied by the carbon dioxide = 3·7581 − 0·7177

= 3·0404 c.c.

Density of carbon dioxide at −115·2° C $= \dfrac{\text{Weight}}{\text{Volume}}$

$= \dfrac{4·8939}{3·0404}$

= 1·6096

The following Tables V and VI show the results obtained with two different samples of propane.

Table V.—Sample A.

Weight of Propane = 0 4767 gms

Weight of Carbon Dioxide . = 4 8939 gms.

Temperature	Volume, Carbon Dioxide and Propane	Density, Propane	Volume, Propane	Volume, Carbon Dioxide	Density, Carbon Dioxide
(° C)	c c		c c	c c	
− 81 5	3 879	0 627	0 760	3 119	1 569
− 83 6	3 869	0 629	0 758	3 111	1 573
− 85 5	3 863	0 631	0 755	3 108	1 575
− 95 3	3 823	0 642	0 742	3 081	1 589
−105 2	3 788	0 653	0 730	3 058	1 600
115 2	3 758	0 664	0 718	3 040	1 610
−128 8	3 722	0 679	0 702	3 020	1 621
−183	3 588	0 739	0 645	2 943	1 663

Table VI —Sample B

Weight of Propane = 0 2736 gms

Weight of Carbon Dioxide = 5 3352 gms

Temperature	Volume, Carbon Dioxide and Propane	Density, Propane	Volume, Propane	Volume, Carbon Dioxide	Density, Carbon Dioxide
(° C)	c c		c c	c c	
− 79 6	3 847	0 625	0 438	3 409	1 565
− 87 9	3 804	0 634	0 432	3 373	1 582
− 95 1	3 782	0 642	0 426	3 356	1 590
−105 1	3 749	0 653	0 419	3 330	1 602
−114 9	3 723	0 664	0 412	3 311	1 611
−125 2	3 694	0 675	0 405	3 288	1 623
−135 2	3 672	0 686	0 399	3 273	1 630
−183	3 557	0 739	0 370	3 187	1 674

It is interesting to note that Behn obtained a value of 1 56 for the density of solid carbon dioxide at −79° C, this being the only temperature at which it was determined *

The densities given in the above tables are shown in fig 5, where *D* represents the density and T represents the temperature in degrees Centigrade The values obtained with Sample A (Table V) are designated by the circles enclosing crosses while the plain circles mark those found for Sample B (Table VI)

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* ' Ann. d. Phys.,' vol 3, p. 735 (1900)

By drawing tangents to this curve the coefficient of expansion of solid carbon dioxide was obtained

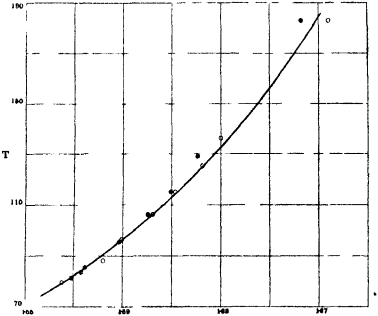

Fig 5

In Table VII the expansion coefficients are given in column 3 and it will be seen that they are much greater than those of most solids

Table VII

Temperature (° A)	C_p (Atomic)	$3a$ (Cubical)	C_v (Atomic)	C_v (Molecular)
183	0 301	0 00128	0 222	9 77
175	0 288	0 00118	0 223	9 81
171	0 282	0 00101	0 233	10 25
165	0 273	0 00096	0 232	10 21
155	0 262	0 00091	0 227	9 99
131	0 244	0 00063	0 220	9 68
109	0 240	0 00060	0 222	9 77

Grüneisen has shown that the molecular heat at constant pressure can be related to that at constant volume by means of the compressibility and expansion coefficients in the following way

$$C_p = C_V\left(1 + \frac{9T\alpha^2V}{KC_V}\right),$$

where

C_p is the molecular heat at constant pressure
C_V is the molecular heat at constant volume
T is the absolute temperature
α is the linear coefficient of expansion
V is the molecular volume
K is the compressibility

Now if $\frac{V}{KC_V}$ can be put equal to some constant k* then

$$C_p = C_V\,(1+9kT\alpha^2)$$

using the extreme values of C_p, T and α in Table VII, and assuming C_V to be the same in both instances, k is found to be equal to 1197 and C_V (atomic) is shown to have the values given in column 1 of Table VII

These values given an average for C_V (molecular) over the temperature range 183° A to 109° A of 9 9 calories, which is considerably lower than the value for C_p and more of the order of magnitude that one would expect Taking the values of Koren† for $CaCO_3$ and CaO over a similar temperature range, the molecular heat for the bound CO_2 comes out to be 6 4 calories The high values for the specific heat at constant pressure obtained for carbon dioxide may therefore be ascribed to its enormous expansion coefficient and probably its correspondingly high compressibility

V - *Summary and Conclusion*

The specific heat of solid carbon dioxide was measured over the temperature range 194 5° A to 90° A, and that of the liquid from 298° A to 194 5° A

The latent heats of fusion and sublimation were determined directly and the latent heat of evaporation was calculated

As a test of the accuracy of the calorimetric measurements it is of interest to compare the latent heat of sublimation of the solid with that calculated from the Clausius-Clapeyron equation From density measurements of gaseous carbon-dioxide at low temperatures made in this laboratory* the weight of one litre of the gas at −78 5° C was found to be 2 840 grams The vapour pressure was taken from the measurements of Henning and Stock† and the calculated value for the latent heat of sublimation was 137 7 calories per gram This figure agrees to within 0 6 per cent of the result obtained directly, namely, 136 9 calories per gram

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* W C McC Lewis, 'System of Physical Chemistry,' vol 3 p 65 (1919)

† 'Ann d Phys.,' vol 36, p 49 (1911)

The expansion coefficient of the solid was shown to be abnormally large, and values of so-called molecular heat at constant volume were calculated on the basis of several assumptions which, in the opinion of the authors, invalidate the accuracy of the absolute values They do show, however, that the abnormally high results for the molecular heat at constant pressure are connected with this expansion coefficient

The calculation of Trouton's constant from the date contained in this paper gives it a value of 20 7 which places carbon dioxide in the liquid state among the unassociated normal liquids

It would be of considerable interest to determine the crystal structure of the solid because the expansion coefficient (especially near its melting point) is greater than that recorded for any other solid Probably the abnormally high vapour pressure of the solid is connected with this fact

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* Maass and Mennie, ' Roy. Soc Proc ,' A, vol 110, p 198 (1926)

† ' Zeit Phys ,' vol. 4, p 226 (1921)

A Homogeneous Unimolecular Reaction—the Thermal Decomposition of Acetone in the Gaseous State

By C N Hinshelwood, Fellow of Trinity College, Oxford, and W K Hutchison, Scholar of Corpus Christi College, Oxford

(Communicated by Prof J W Nicholson, F R S —Received Feb 17, 1926)

Unimolecular reactions in gases have a rather exceptional theoretical interest, because they involve, apparently, the spontaneous change of isolated molecules One example only has been satisfactorily investigated, the thermal decomposition of nitrogen pentoxide,* and an examination of the molecular statistics of this reaction leaves a certain mystery about the method by which the molecules are caused to decompose It is unwise to infer too much from what might be a quite special instance, hence we have during the last few years searched for other examples We now find that the thermal decomposition of acetone vapour satisfies the experimental criteria of a homogeneous, unimolecular reaction Moreover, the peculiarities of the nitrogen pentoxide decomposition are here reproduced, although the absolute temperature at which the acetone decomposition can be studied is approximately three times as high as that at which nitrogen pentoxide reacts with conveniently measureable speed Since then this analogy exists between the two reactions, taking place at such different temperatures, we may begin to draw theoretical conclusions with more confidence

The theoretical discussion is reserved for the last section, after the experimental work has been described, because the conclusions depend very much upon the actual numerical results

Experimental Procedure—The velocity of decomposition of acetone is conveniently measurable between 500° and 600° C The reaction vessel was a silica bulb heated in an electric furnace, the temperature of which was measured by means of a platinum-rhodium thermocouple In a number of experiments confirmatory readings were taken with another thermocouple of base metal The temperature could be kept constant within about one degree The decomposition was followed by observing the increase of pressure with a capillary mercury manometer The arrangement of the apparatus is obvious from fig 1, but a few special points call for comment Connection between the silica bulb and the glass parts of the apparatus was made by means of finely-ground flanges which could be screwed tightly together They were about 20 mm broad and with their outer edges very slightly lubricated held vacuum perfectly when heated All parts of the apparatus which projected from the furnace had to be kept at a temperature above the condensing point of acetone namely about 40° C under the conditions of the experiments The capillary tubes including the manometer were heated by means of resistance wire and the flanges by means of a small tubular electric furnace. An extremely well ground capillary tap was used and with a thin layer of rather stiff lubricant showed no tendency to leak when warm The bulb A contained very pure liquid acetone and vapour at any desired pressure could be let into the reaction vessel through the tap if the temperature of the

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* Daniels and Johnston, 'J Amer Chem Soc,' vol. 43, p 53 (1921)

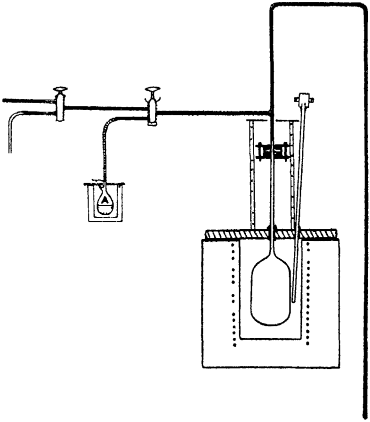

Fig 1

furnace heating A was suitably adjusted Readings of time and pressure could then be taken in the obvious manner.*

Evidence that the Reaction is Unimolecular and Homogeneous.—The experimental criteria of a unimolecular homogeneous reaction are (*a*) that the time taken for any fraction of the total change to complete itself is independent of the initial pressure, and (*b*) that variation of the amount of surface exposed to the gas leaves the reaction velocity unchanged Both these conditions are shown to be fulfilled by the following results

Table I

Temperature °C	Initial pressure in mm	t_1 seconds.	t_2 seconds	t_3 seconds
578	385	100	275	754
	362	91	260	655
	189	92	270	700
	112	103	275	620
601	362	26	77	199
	296	27	80	200
	230	24	85	240
	192	20	78	—
	98	30	86	222

t_1, t_2, and t_3 are the times in seconds required for the pressure to increase by 25 per cent, 50 per cent, and 75 per cent respectively, of its initial value Condition (*a*) is thus fulfilled

The following table provides further confirmation and shows that condition (*b*) is fulfilled also

Table II

Temperature °C	Initial pressure in mm	t_2 seconds	
596	401	117	Bulb empty
	297	100	
	272	130	
	265	132	
	208	125	
	190	111	
	Average	119 *seconds*	
596	420	124	Bulb about ½ full of coarse silica powder
	410	114	
	406	122	
	339	114	
	298	109	
	212	107	
	Average :	115 *seconds*	

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* For details *cf.* 'J Chem Soc.,' vol. 125, p 396 (1924)

The addition of silica powder to the bulb produces no effect at any stage of the reaction. For example, the average values of the time required for a 25 per cent increase of pressure in the above experiments were

without silica powder, $t_1 = 34$ seconds
with ,, $t_1 = 37$ seconds

At lower temperatures the reaction remained homogeneous, as shown below

Table III

Temperature °C	Initial pressure	t_2 seconds	
516	304	2,370	Bulb empty
	301	2,400	
	300	2,080	Bulb containing silica powder
	301	2,390	

Influence of other Gases—In order to find the effect of foreign gases on the rate of reaction, a number of experiments were made by introducing carbon monoxide into the reaction vessel This gas was chosen as it was the major product of the reaction

Table IV

Temperature °C	Pressure of CO added	Initial pressure of Acetone	t_1 seconds.	t_2 seconds
589	Nil	244	53	154
	Nil	226	59	168
	205	243	53	165
	210	177	52	162
	316	228	50	154

The influence is inappreciable Nitrogen was found in a similar way to have no effect

Nature and Course of the Decomposition—We have now shown that the decomposition of acetone vapour is a homogeneous reaction which satisfies the chief experimental criterion of a unimolecular change We should therefore be able to calculate the unimolecular velocity constants. For this purpose it is essential to know the limiting value of the pressure increase attending the decomposition. We can hardly expect the experimentally observed "end-point" to be the proper value for insertion in the unimolecular equation, because the hydrocarbons produced in the primary decomposition of the acetone undergo slow subsequent reactions, continuing after all the acetone is decomposed. It is, in fact, found that the curve obtained by plotting pressure increase against time does not become parallel to the time axis, but continues with a small upward slope, after it is obvious that the main reaction is over. A correction for this is easily applied in a way which is illustrated in fig. 2. Curve I is the experimental curve, which does not become quite horizontal in the normal way. The line AB, to which the curve is asymptotic, is drawn, and produced to meet the pressure axis at A. The vertical distance between AB and the horizontal line AC at any time, gives the pressure increase attributable to the subsequent reactions. By subtracting these values from the ordinates of curve I curve II is obtained, which is the ideal decomposition curve of the acetone, and is asymptotic to the horizontal line AC, which represents the true end-point of the reaction. It will be seen that the corrections are not large over the first 70 per cent or 80 per cent of the course. The following table shows the method of calculating the constant. The experiment was made at 534° C.

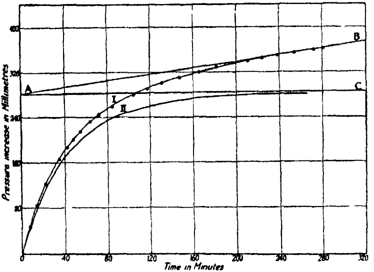

FIG. 2

Time in minutes t	Pressure increase	Corrected pressure increase.	$1/t \log_{10}\left(\frac{284}{284 - x}\right)$
		x	
10	64	60	0 0103
20	115	108	0 0104
30	152	143	0 0101
40	182	171	0 0100
50	205	193	0 0099
60	225	210	0 0098
80	255	235	0 0095
100	277	250	0 0092
120	292	259	
140	308	267	Average: 0 0099
180	328	277	
220	344	281	The corresponding value of k
250	354	282	with natural logarithms and
280	363	283	the time in seconds is—
∞	—	284	0 000380

It is evident that we can in this way find the velocity constant, but the proof that the reaction is unimolecular is, of course, independent of the mere constancy of these figures

The following values of k were obtained in this manner at 578° C

Initial Pressure of Acetone	k
362	0 00348
189	0 00311
112	0 00339

Seconds and natural logarithms are used

In what follows experimental results will generally be recorded in terms of the time required for the pressure to increase by 50 per cent or some other definite fraction of its initial value The relation between such times and the velocity constant is given by the equation

$$k = \frac{1}{t_2} \log C_1 = \frac{1}{t_2} \log C_2, \text{ etc.},$$

where C_1, etc , are constants For values of t_2, corresponding to 50 per cent increase, we find, independently of temperature

$$k = \frac{0\ 901}{t_2}$$

Analysis of the Products of Reaction.—It is first important to mention that the corrected "end-points" obtained by the method of the last section are independent both of the temperature and of the presence of silica powder.

For example, 369 mm. of acetone at 534° C gave a corrected end-point of 284 mm increase, or 77 per cent, and in a similar experiment at 578° C the corrected end-point increase amounted to 79 per cent Over this range of temperature the velocity varies about tenfold This, as far as it goes, indicates that the nature of the reaction whose velocity we are measuring does not vary appreciably with temperature, but it was desirable to confirm this by analysis of the products of reaction. A number of analyses made at different temperatures and at different stages of the charge showed definitely that the mode of decomposition is always the same

The essential part of the primary decomposition is the separation of carbon monoxide from the molecule, leaving two methyl residues, the interaction of which determines the other products The simplest possible result would be their union to form ethane, but the application of Nernst's heat theorem shows that methane is the stablest of the hydrocarbons at these temperatures It is not therefore surprising that the result is by no means ethane alone, but a little ethylene, some free carbon, and principally a mixture of saturated hydrocarbons and hydrogen, the composition of which averages out almost to that of pure methane This corresponds with what Sabatier found in the catalytic decomposition of acetone ('La Catalyse en Chimie Organique,' 1920, p 237) A small amount of carbon dioxide was formed, which may well have come from the subsequent separation of carbon from carbon monoxide The amount of tarry condensation products was surprisingly small, the reaction bulb never requiring to be cleaned The following figures illustrate the main point, namely, that the course of the reaction is independent of temperature

Percentage	Temperature 578° C		Temperature 534° C	
	Half way through reaction	At end of reaction	Half way through reaction	At end of reaction
CO_2	4·6	6·8	7·9	
C_2H_4	10·7	6·8	10·6	4·9
CO	35·2	32·6	33·2	32·8
Saturated hydrocarbons + H_2	49·5	51·8	48·3	

A special analysis was made of the "Saturated hydrocarbons and Hydrogen" by combustion The results were constant. The following is a typical one, belonging to the first analysis in the above table.

One volume of the mixture, when burnt with air, gave a contraction of 1 82 volumes, and 0 88 volumes of carbon dioxide were formed. Were the gas pure methane, the contraction would have been 2 00 volumes, and the volume of carbon dioxide 1 00

The figures corresponding to the second analysis are 1 91 volumes contraction and 1 03 volumes carbon dioxide

The Temperature Coefficient and the Heat of Activation —Since we have shown that the course and nature of the reaction are the same at different temperatures, we can calculate the heat of activation directly from the experimentally observed velocities In order to leave no doubt that the heat of activation refers to nothing but the primary unimolecular decomposition of the acetone molecule, the following method of calculation was adopted

Let t_1, t_2, and t_3 be, as before, the times required for the total pressure in the decomposition vessel to increase by 25 per cent, 50 per cent and 75 per cent respectively, of its initial value Plotting the logarithms of these times against the reciprocal of the absolute temperature, three straight lines are obtained, the slopes of which determine values of the heat of activation If they were not all equal, we could extrapolate, and determine the heat of activation corresponding to the initial reaction. But these three lines are almost exactly parallel, as shown in fig 3, and values of the heat of activation calculated from them are as follows —

E from t_1	68,600 cal
E from t_2	68,200 cal
E from t_3	64,200 cal

The value obtained from the t_3 curve is naturally a little inaccurate for reasons which will be obvious from the previous sections We may therefore take the average of the first two values and adopt as the best value for the heat of activation —

$$E = 68,500 \text{ cal to the nearest } 500 \text{ cal}$$

The results upon which the above calculations depend are summarised in Table V below

Two experiments were performed at each temperature The results may be summarised in the formula

$$\frac{d \ln k}{dT} = \frac{68,500}{RT^2}$$

Therefore

$$\ln k = \text{Constant} - \frac{68,500}{RT}.$$

Table V

T (abs)	Mean t_1 seconds	Mean t_2 seconds	Mean t_3 seconds
904 5°	7 4	24 5	85 5
800	14	53	158
874°	26	81 5	240
857°	72	207	526
842°	119	409	1 090
824	366	1 044	2 442
809°	668	1 950	4 680
790	1 890	5 640	11 880
779	4 500	12 420	

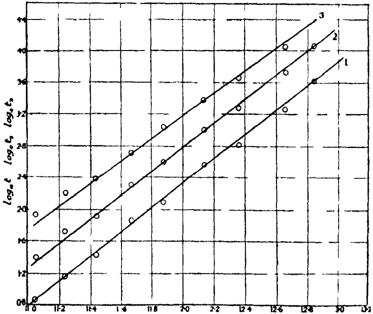

FIG 3—Influence of Temperature on Rate of Homogeneous Unimolecular Decomposition of Acetone in the gaseous state

Line 1 refers to t etc

The experimental points in fig 3 lie closely on the lines so that we may determine the value of the constant by reading off the value of t corresponding to any standard temperature At 550° C the value of t_2 read from the middle curve is 1075 seconds The corresponding value of k as previously shown, is therefore $\frac{0\ 901}{1075} = 0\ 000837$ Whence we find that the above equation becomes

$$\ln k = 34\ 95 - \frac{68{,}500}{RT}$$

If t_2 is required it is found from the formula $k = 0\ 901/t_2$ The following typical examples illustrate the extent to which the formula is applicable —

T (abs)	t_2 (calc)	t_2 (obs)
904 5°	24″	24″ and 25″
857°	200″	203″ and 211″
809°	2240″	1950″ and 1950″

Theoretical discussion —One of the most significant points about bimolecular reactions in gases is that the heats of activation form a regular series increasing parallel with the temperature at which the velocity constant attains some assigned value It can be shown that the number of molecules reacting is given by the expression

$$\textit{number of collisions} \times e^{E/RT}$$

multiplied by a factor which is not much less than unity * Since the number of collisions is not very different in different gases and at different temperatures the rate of a bimolecular reaction is governed mainly by the factor $e^{E/RT}$ so that for equal values of the velocity constant E is nearly proportional to T If the velocity of reaction were governed by any entirely specific factor other than E this proportionality could not exist In this sense therefore proportionality of E and T in reactions of a given kind indicates that the molecules are activated by analogous processes There is evidence that the proportionality is also found in termolecular reactions † but there has been no other unimolecular reaction suitable for comparison with the nitrogen pentoxide decomposition ‡ The heat of activation in this reaction is given by Daniels and Johnston as 24 700 calories At 55° C the velocity constant is 0 00150, with the time expressed in seconds The value of k for the acetone decomposition reaches this value at 562° C The ratio of the absolute temperatures is thus $\frac{835}{328} = 2\ 55$ In keeping with this the heat of activation in the acetone decomposition is very much greater than that of the nitrogen pentoxide decomposition. We have

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* *Cf* J Chem Soc vol 125 p 1841 (1924) Phil. Mag vol 50 p 1135 (1925)

† J Chem Soc (1926)

‡ *Loc. cit supra*

Decomposition of	T (abs.)	E	E RT
N_2O_5	328	24,700	38 0
CH_3COCH_3	835°	68,500	41 4

The parallelism is sufficiently obvious

The position of the theory of unimolecular reactions may be summarised as follows —

(1) Perrin's argument* that the molecules must be activated by radiation since the velocity constant is independent of concentration, and therefore of collisions, can be met by (*a*) the Christiansen chain mechanism† and by (*b*) Lindemann's suggestion‡ that activation and de-activation take place at a rate which is very large compared with the velocity of reaction The chain mechanism is very improbable in reactions which are not much influenced by the presence of foreign gases, and therefore in the decomposition of nitrogen pentoxide and of acetone

(2) Even if activation resulted in immediate reaction, it has been shown that the energy of activation cannot be communicated to molecules of nitrogen pentoxide by collision rapidly enough to account for the observed rate of change.§ Thus (*b*) of the last paragraph seems to be inapplicable, and we are left with the probability that the molecules become activated by the absorption of radiation

(3) The theory of activation by radiation of a narrow range of frequency is untenable ||

(4) The only question which arises when activation by a large continuous range of frequencies is supposed, is whether the energy can be communicated to the molecules rapidly enough The plain truth about this is that, in the present state of the theory of radiation, the question cannot be answered As, however, this seems to be most probably the way in which the molecules of nitrogen pentoxide are activated, we should be justified in adopting it as a

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* 'Ann Phys,' vol. 11, p 1 (1919)

† 'Z physical Chem,' vol 104, p 451 (1923)

‡ 'Trans Faraday Soc,' 1922, vol 17, p 598

§ *Cf* Tolman, 'J Amer Chem Soc,' vol 47, p 1524 (1925)

|| *Idem, ibid*

hypothesis, if the study of other unimolecular reactions led to the same conclusion.

E/RT for the acetone decomposition being greater than the value for the nitrogen pentoxide decomposition, activation of the molecules by any mechanism will be more difficult, since the probability factor $e^{-E/RT}$ appears in the distribution law of all forms of thermal energy Thus the activation of the acetone molecules by collision seems to be impossible. The simplest way of showing this directly is as follows

The rate of activation by collision in a unimolecular reaction with heat of activation E, cannot be greater than the rate of a bimolecular reaction in which the sum of the energies of activation of the two molecules is E, and every collision between activated molecules is effective* Indeed it could only be equal to this, if the joint energy of the two molecules were all communicated in the collision to the one which reacts The maximum rate of activation thus appears to be

$$\sqrt{2}\,\pi\,\bar{u}\,n^2\,\sigma^2\,e^{-E/RT}$$

In the present example we have $\sigma =$ the diameter of the acetone molecule, and may be taken as approximately 5×10^{-8} cm

$\bar{u} =$ the root mean square velocity, and at 835° Abs is $5\ 99 \times 10^4$ cm /sec.

$n =$ the number of molecules per c c and at 835° Abs and 760 mm pressure is $8\ 85 \times 10^{18}$

Substituting these values in the above equation, the maximum number of molecules in one cubic centimetre which could be activated by collision per second is $0\ 54 \times 10^{11}$

Taking the value of k at 835° Abs as 0 00150, the number of molecules in one cubic centimetre at 760 mm reacting per second is

$$1\ 33 \times 10^{16},$$

Thus the number of molecules reacting appears to be about 10^5 times greater than the number which could be activated by collision. This number is far too large to be accounted for by any minor error such as the very rough value taken for the diameter of the acetone molecule

It seems then that we must adopt some generalised form of the radiation theory, but whether this interpretation is finally confirmed, or whether it has to be modified, the important positive fact is, that any modification will be equally applicable to both the unimolecular reactions under consideration

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* *Cf* 'J Chem. Soc,' vol 125, p. 1846 (1924)

Summary

The thermal decomposition of acetone vapour is a homogeneous, unimolecular reaction, and has been investigated over the temperature range 506°–632° C.

The heat of activation is 68,500 calories, and the results can be summarised by the equation

$$\ln k = 34.95 - \frac{68{,}500}{RT}$$

Calculations show that the number of molecules reacting per second is about 10^5 times greater than the maximum number that could be activated by collision. The absolute rate at 835° Abs is the same as that of the nitrogen pentoxide decomposition at 328° Abs, the value of E/RT being nearly the same in these two reactions, for these two temperatures

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Gaseous Combustion in Electric Discharges.—Part I. The Combustion of Electrolytic Gas in Direct Current Discharges

By G. I. Finch and L. G. Cowen

(Communicated by Prof. W. A. Bone, F.R.S.—Received February 18, 1926.)

[Plate 5.]

Introduction

In connection with the researches upon various aspects of gaseous combustion which are being carried out in the Department of Chemical Technology, Imperial College of Science and Technology, South Kensington, one of us (G. I. F.) has undertaken a systematic investigation of the mechanism of combustion as initiated by, or occurring in, electric discharges. The present paper embodies the results of our experiments upon the combustion of electrolytic gas in direct-current discharges

Three phases have been distinguished in the process of gaseous combustion, namely, (i) a slow (non-self-propellant) combustion below the ignition point, (ii) a self-propellant flame propagation, and (iii) sometimes, also, a short preflame period during which combustion is self-propellant. The point at which the process becomes self-propellant is sometimes termed the "ignition point." Before combustion can be determined in it, however, energy in some form or other must be imparted to a given combustible system from an external source. Frequently, heat energy is so supplied, in which case it is customary to speak of an ignition temperature; on the other hand, electrical energy may be supplied, *e.g.*, by a spark, in which case we speak of a minimum igniting energy or minimum igniting current being necessary to make the combustion self-propellant. In such conditions, whilst the self-propellant stage of combustion is usually determined by the purely electrical properties of the discharge employed (even though it may be affected by other influences, such as pressure waves emanating therefrom), yet, having once been set up, it is subsequently propagated through the system independently of such properties. On the other hand, the pre-ignition or non-self-propellant stage is throughout intimately associated with and determined by the discharge itself. Hence, an experimental examination of the influence of electric discharges upon the pre-ignition stage of combustion in gaseous mixtures may be expected to reveal the nature and mechanism of electrical ignition, and indeed of the process of combustion as a whole.

Kirkby* has studied the effect of steady direct-current electric discharges on electrolytic gas at pressures below that at which ignition can occur. He found (provided that the circumstances of the discharge, including pressure, current, and degree of separation of the electrodes were constant) that the amount of water formed was proportional to the quantity of electricity passed in the discharge, and independent of the nature of the electrodes, and "that the chemical action took place at all points of the discharge."

As far as we are aware, with the exception of the above, all other investigations of the effect of electric discharges upon the pre-ignition stage of gaseous combustion have been limited to the determination of the minimum igniting energy or current. Sometimes, however, the experimental results have been contradictory, or difficult to interpret, because of the fact that the types of electric discharges employed have involved the introduction of unknown factors (both electrical and otherwise) which have obscured the issues.

Low-tension discharges were first employed by Prof. W. M. Thornton,† and to him we owe the first proof of the significance of what he termed "the least igniting current" for various combustible gaseous mixtures. Both direct and alternating currents were used The discharge was produced by opening a circuit in which a known current was flowing In neither case was the rate of dissipation of energy in the discharge constant, it attained a maximum at or shortly after the beginning of the opening of the circuit and fell with widening of the gap to a minimum, which was followed by extinction of the discharge The total amount of energy dissipated was unknown Although the current flowing prior to opening the circuit was known, it could not, as Thornton pointed out, in the case of direct current be assumed to be equal to the maximum that passed in the discharge itself With alternating currents, additional complications arose in that the value of the maximum current also depended upon the phase angle and frequency of the supply, as well as upon the actual moment at which opening of the circuit began Thornton* showed that the nature and condition of the material of which the electrodes consist have a pronounced and, at times, somewhat erratic influence on the experimental results obtained with such "break sparks" The region of the discharge, particularly when passing in a gas under normal pressure, is a zone of high temperature and contains the vapour of the electrode material The discharges produced in electrical bell signalling circuits, such as have been investigated by Morgan,† are low-tension discharges similar in character to those discussed above

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* 'Phil. Mag.,' vol. 7, p. 223 (1904); vol. 13, p. 289 (1907); 'Roy. Soc. Proc.,' A, vol. 85, p. 151 (1911).

† 'Inst. Mining Eng. Trans.,' p. 145 (1912).

Besides Thornton,‡ Morgan and Wheeler§ have studied ignition by high-tension discharges produced by means of an induction coil or magneto across a fixed gap Taylor Jones‖ has examined in detail the extremely complex nature of this type of discharge, which is oscillatory, a single discharge consisting of a train of sparks Morgan,¶ and Patterson and Campbell** have shown that the igniting power depends solely on the energy associated with the first oscillation, and not on the total energy dissipated in the complete train of oscillations of a single discharge The rate of dissipation of energy is not constant, and the maximum and mean currents thereof are difficult to ascertain without a suitable oscillograph Furthermore, as has been shown by Prof H B Dixon,†† in addition to the presence of electrode material vapour in the discharge, intense pressure waves are set up in the surrounding gas The discharge is also characterized by a high temperature

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* 'Brit Assoc Adv Sci Rept.,' p. 469 (1923)

† 'J Chem Soc,' vol 115, p 94 (1919)

‡ 'Roy Soc Proc,' A, vol 92, p 381 (1916)

§ 'J Chem Soc,' vol 119, p 239 (1921)

‖ 'The Theory of the Induction Coil' (1921).

¶ 'Principles of Electric Spark Ignition'

** 'Proc Phys Soc,' p 177 (1919).

†† 'Phil. Trans,' A, vol 200, p 315 (1903)

The high-tension capacity discharge, produced by discharging a condenser across a fixed or closing gap, resembles the first part of the induction coil or magneto discharge The rate of dissipation of energy is again not constant, but the total energy dissipated in all the oscillations of a complete train and the maximum current of the first oscillation can be readily ascertained On the other hand, the capacity discharge gives rise to disturbing non-electrical phenomena similar to, but, as a rule, more intense than, those of the induction coil discharge, being hot, containing metal vapour, and giving rise to pressure waves in the surrounding gas

Thus the use of any of the above types of electric discharges necessarily introduces not only electrical effects which may be difficult to control and are not readily amenable to exact measurement, but also disturbing non-electrical phenomena which may tend to mask the purely electrical effects of the discharge itself.

In studying the electrical ignition of gases, the investigators referred to were chiefly concerned with the examination of such conditions as arise in ignition either in internal combustion engines or in coal mines, and the types of electric discharges investigated were selected as closely reproducing those occurring in actual practice For the purpose of quantitatively investigating the electrical effects of electric discharges upon the pre-ignition stage of combustion, however, the discharge should be such that the current and rate of dissipation of energy are constant and that the non-electrical phenomena with which the electric discharge is ordinarily associated should be either eliminated or reduced to a minimum

If, as was done in Kirkby's experiments, the necessary potential be furnished by an accumulator battery in series with a resistance to the electrodes of a suitably evacuated discharge tube, a discharge occurs, the luminous positive column of which is broken up into striations If, after the discharge has commenced, the current be such that the fall in the voltage-current characteristic is steep, an examination of these striæ by means of a mirror revolving at a suitable speed shows that they flicker, in spite of the fact that the electromotive force of the accumulator battery is constant. This flickering or, rather, waxing and waning of the light emitted by the luminous striæ is due to capacity in the circuit, and differs both in appearance and nature from the type of discontinuity described by Prof Whiddington, F.R.S.,* which is practically independent of any capacity included in the circuit. If, however, steps are taken to eliminate as far as possible the effects of stray capacity of the leads passing to the electrodes and of the electrodes themselves, the light emitted by the striations becomes so steady that a flickering, even in the region of steep characteristic, can no longer be detected. The current and rate of dissipation of energy in the discharge are then practically constant, and both may be readily determined and controlled. By suitably altering the shape of the electrodes and their degree of separation, a steady discharge may, in the same manner, be maintained at more elevated gaseous pressures. Thermal effects of the discharge may be reduced by diminution of the pressure of the gaseous mixture in which the discharge is maintained and by employing small currents. Further, the use of suitable electrode materials will greatly assist in keeping the discharge free from metal vapour. Pressure waves are not set up by a steady discharge.

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* 'Nature,' vol. 116, p 507 (1925).

Experimental.

In the experiments about to be described it was our aim to arrange conditions in such a manner as to eliminate as far as possible any chemical combination, including that due to heat, other than that caused by the ionisation of the gas, and then to study the proportionality, if any, observed between the rate of chemical change and the current or rate of dissipation of electrical energy. We have been able to realise conditions under which the rate of steam formation, resulting from the passage of an electric discharge in electrolytic gas at pressures where ignition can occur, is directly proportional to the current passing and quite independent of (i) potential fall between the electrodes, (2) gas pressure, and (iii) temperature. We believe that this is the first time that such a direct relationship has been established in the case of an electric discharge in an explosive gaseous mixture. In these experiments, steady electric discharges were passed through electrolytic gas at pressures between 20 and 100 mm. throughout which range the gas is explosive, the maximum rate of dissipation of energy being in excess of 3·8 watts.

Description of the Electrical Circuit (fig. 1).

The current was supplied by the rotary transformer, T, by means of which the 220-volt direct-current supply from the mains was converted to a high-tension direct current. As the pressure of the mains was apt to fluctuate, it was steadied by means of the floating accumulator battery, B, shunted across the mains. The constancy of the steadied pressure was observed by means of the voltmeter, V. The input terminals of T were connected with B through the ammeter, A, and the variable resistance, R. The speed and hence the output pressure of T could be controlled by means of R. The normal speed of T was

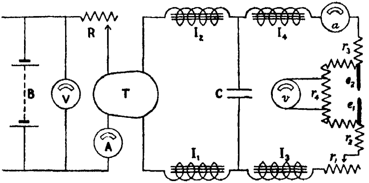

Fig. 1.

from 2,200 to 3,500 r.p.m. according to the output required. The output commutator had 64 segments. Examination of the discharge produced by the high-tension output current by means of a revolving mirror showed pronounced commutator ripple and also occasional irregularities, the latter probably due to slight intermittent sparking at the high-tension brushes. The remainder of the circuit now to be described was intended to smooth out these ripples and irregularities, and to supply a steady pressure to the electrodes. The high-tension output terminals of T were connected through the large chokes I_1 and I_2, the inductance and resistance of each being 55 henrys and 9,000 ohms, respectively, to the terminals of the condenser, C, of 2 microfarads capacity. One terminal of C was connected through (i) the choke, I_3, the inductance and resistance of which were 70 henrys and 12,000 ohms, respectively, (ii) the non-inductive liquid resistance, r_1, which was variable in steps of 100,000 ohms from 0 to 1 megohm, and (iii) the non-inductive resistance, r_2, of 50,000 ohms to the electrode, e_1. The other terminal of C was connected to the second electrode, e_2, through the choke, I_4, similar to I_3, the moving coil milliammeter, a, and the resistance, r_3, similar to r_2. The electrodes were shunted by the non-inductive 20 megohm resistance, r_4, across two tappings at a suitable distance apart, on either side of the centre of which was shunted the electrostatic voltmeter, v. These last-mentioned resistances were connected through the shortest possible leads to the electrodes with the object of reducing capacity effects on the electrode sides of r_2, r_3 and r_4 to a minimum. The milliammeter indicated the currents passing r_4 and the discharge between e_1 and e_2. The readings were duly corrected in order to obtain the value of the current carried by the discharge alone The corrections were small and, as a rule, negligible The rotary transformer could maintain, on an open circuit, an output pressure of 1,500 volts between the electrodes With a discharge passing and a potential drop of 550 volts between the electrodes, the transformer was capable of furnishing a steady current of about 6 milliamperes, which value could not be much exceeded for any length of time without serious risk of damage to the transformer Both sides of the high-tension circuit were carefully insulated from each other and from earth

The Combustion Chamber (fig 2)

The combustion chamber consisted of a glass vessel fitted with a two-way tap, one branch of which was connected to the electrolytic gas supply, the other to a "Hyvac" oil pump A length of copper wire, No 12 S W G, was sealed with sealing wax into each of the glass sleeves, *s*, which, in turn, were secured with sealing wax into the two tubes, *t*, let in at the top of the combustion chamber at an angle to each other By raising or lowering the sleeves, the points of the electrodes could be set to any desired degree of separation Each of the electrodes, e_1 and e_2, consisted of a 1 cm length of No 20 S W G wire, soft-soldered to the end of the stout copper wire passing into the combustion chamber The free ends of the electrodes were pointed and finally polished on a buff to a blunt-pointed cone 1 mm in height After being freed from all traces of grease, the electrodes were "run in" by maintaining between them a discharge of 4 to 5 milliamperes in electrolytic gas under a pressure of approximately 90 mm until, with the discharge still passing, the point of the cathode was seen to be uniformly surrounded by a perfectly steady cathode glow Prior to this "running in," the cathode glow (and, to a less extent, the anode glow) showed a tendency to wander along the electrode to and from the point, thus causing variations in the effective degree of separation of the electrodes A U-tube manometer, one limb of which was closed, was sealed into the base of the combustion chamber After filling the manometer with mercury, 27 c c of concentrated sulphuric acid were

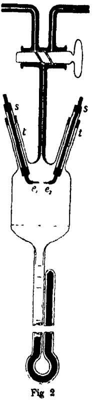

Fig 2

pipetted into the combustion chamber. When the closed limb of the manometer was completely filled with mercury (at pressures above 300 mm.), the volume of the free space in the combustion chamber was 108·0 c.c., and 104·5 c.c. when completely evacuated The combustion chamber was surrounded by a water jacket maintained at a constant temperature of 20° C The insulation resistance of the electrodes, when disconnected from the circuit, was tested at frequent intervals by means of a megger at 1,000 volts and was found to be always above 50 megohms This test was carried out with the combustion chamber filled with dry air at normal pressure and water flowing in the water jacket

Preparation of the Gas Mixture

Electrolytic gas, prepared by electrolysis of a solution of thrice re-crystallised barium hydroxide, was used in all experiments The gas was not stored but prepared as and when required for use, and was purified and dried by passage through a spiral washer containing concentrated caustic potash solution followed by two others containing concentrated sulphuric acid. The electrolysers and washers were sealed directly on to the combustion vessel. The purity of the electrolytic gas was frequently checked by exploding a known volume over concentrated sulphuric acid in the combustion vessel and noting the final pressure attained after explosion

The Electric Discharge

Within the range of conditions of current and gas pressure examined in the experiments recorded below, three well-defined zones could be distinguished in the discharge in electrolytic gas, namely, the cathode, anode, and inter-electrode zones. The entire cone of the cathode point was enveloped by a moderately luminous blue glow, the extent of which increased with increasing current but decreased very slightly with increasing gas pressure throughout the range of from 25 to 100 mm For example, with a gas pressure of 45 mm, the length of the cathode, measured from the extreme point, enclosed by the glow was approximately 1 0 mm with a current of 1 milliampere and 1·4 mm. with 6 milliamperes With a gas pressure of 90 mm. and similar currents, the glow extended over 1 0 and 1·3 mm. respectively Under a low-power microscope, the cathode zone could be resolved into a thin, purple layer in immediate contact with the cathode (cathode glow) and an outer, blue glowing layer (negative glow) concentric with but separated from the cathode glow by a dark or, at most, feebly luminous blue layer (Crookes' dark space) (fig 3) On the extreme point of

Fig 3

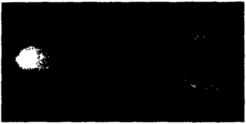

Fig 4

Fig 5

the anode, one minute luminous, reddish white spot (anode glow or spot) or occasionally a close cluster of two or three such spots could be distinguished The space between the cathode and anode zones the inter electrode zone was partly bridged by a bluish purple glow (positive column) which radiated in a fan or brush-shaped manner from the anode glow towards the cathode If the current were allowed to fall to below about 0 8 milliampere the exact value varying somewhat with the gas pressure and possibly also with the nature of the electrode material the discharge changed in appearance the cathode glow becoming less luminous shrinking slightly in thickness but enveloping a greater length of the electrode (fig 5) The anode glow also became appreciably smaller The inter electrode zone however, was almost completely bridged by a slender cone-shaped, bluish purple glow in which minute striæ could occasionally be distinguished The spherical base of the cone was separated from the cathode zone by a narrow dark space (Faraday dark space) but the point of the cone was in contact with the anode glow The transition stage from the first to the second type of discharge is characterised by the appearance of a thin glowing bluish layer situated approximately in the middle of the dark space of the electrode zone (fig 6) We wish to emphasise here that the results obtained by us in studying the effects of the types of discharge shown in figs 4 and 5 upon electrolytic gas are not embodied in this paper but are reserved for a further communication The size and appearance of the electrode zones in both types of discharge were unaffected by a change in the degree of separation of the electrodes alone If the same current were maintained a change in the degree of separation of the electrodes resulted only in an increase in the size of the brush-shaped glow in the inter-electrode zone No difference in the appearance of the discharge could be detected when platinum electrodes were substituted for copper ones It may be reasonably assumed that within the conditions of the experiments to be described below the cathodic fall of potential was practically constant for any given electrode material Revolving mirror examinations of the type of discharge reproduced in fig 3 showed that it was perfectly steady and continuous under all conditions of our experiments

Experimental Procedure

After the electrodes had been sealed in set to a definite gap width and "run in," the combustion chamber was evacuated and the electric discharge started Voluminous diffuse blue glows, that on the cathode being the largest, then enveloped the electrodes and the stout copper wires to which they were soldered The current was now approximately adjusted to the desired value by means of the variable resistance r_1 and electrolytic gas slowly admitted into the combustion chamber until the pressure was just below that, previously determined by experiment, at which either extinction of the discharge occurred through the transformer being unable to maintain the higher voltage now necessary to

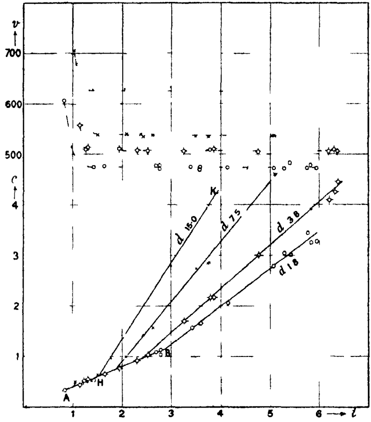

FIG 6.—Copper Electrodes $p = 30$

overcome the increased resistance of the gap or explosion of the mixture took place With admission of the gas the discharge settled down to the region around and between the points of the electrodes assuming the appearance already described and shown in fig 3 It was found essential to start the discharge in the manner described above If the discharge was struck after admission of the gas by applying a sufficiently high voltage to the electrodes either from the transformer or in the event of this not being possible owing to the gap resistance being too great by means of an induction coil it was found that the first rush of current passing at the beginning of the discharge not only disturbed the "run in' condition of the electrodes, but also frequently exploded the gas mixture

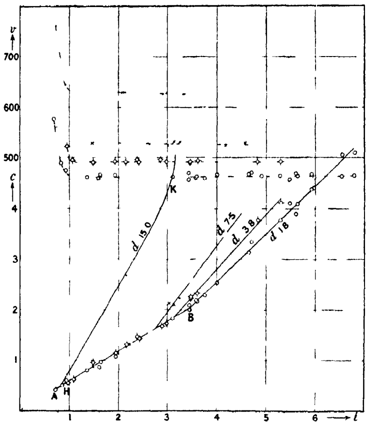

Fig. 7—Platinum Electrodes $p = 30$

At definite intervals (the individual duration of which depended upon the rate of combustion the change of pressure during one such interval being 1 cm or less) simultaneous readings were taken of the gas pressure, current and the potential fall between the electrodes, the observations being continued until the electrolytic gas had been almost consumed Synchronism of the readings was ensured by means of a buzzer signal actuated at definite intervals by a clock This procedure was repeated with various gap widths over a current

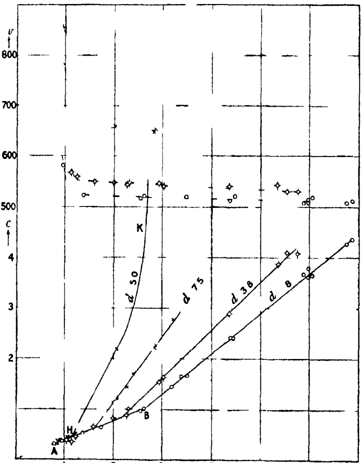

Fig 8 —Copper Electrodes p = 60

range of from 0·8 milliampere to the highest current capable of being furnished by the transformer in most cases below 6 milliamperes From the results obtained a series of curves was plotted connecting the gas pressure with in turn the potential drop across the electrodes current and rate of combustion.

From these curves the voltages currents and rates of combustion corresponding to any required gas pressure and degree of separation of the electrodes could be directly read off

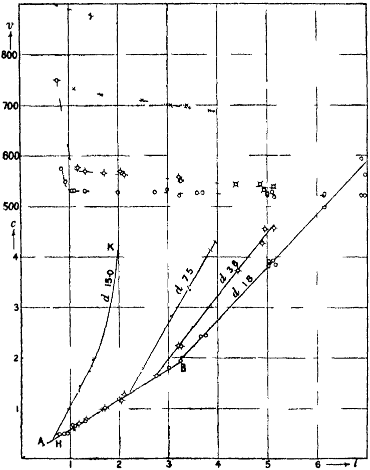

FIG 9 Platinum Electrodes $p = 60$

The sulphuric acid contained in the combustion chamber was replaced with the same volume of fresh concentrated acid at the end of every fifth experiment During each experiment both the discharge and the milliammeter were kept under observation Occasionally in the course of an experiment the anode spot would jump from its normal position on the extreme point to another part of the anode, such movement being accompanied by a sharp kick of the milliammeter needle In such cases the experiment was immediately interrupted, and the electrodes repolished and " run in " prior to starting another

The Experimental Results

Two series of experiments were carried out, one with copper, the other with platinum electrodes With the exception of those corresponding to pressures of 30 and 60 mm , which are shown graphically (figs 6, 7, 8, and 9), the results obtained over a pressure range of from 30 to 90 mm and with varying degrees of separation of the electrodes are tabulated below (Tables I to VI) The notation of the tables is as follows --

p = pressure of electrolytic gas in millimetres of mercury

d = degree of separation of electrodes in millimetres

v = potential fall between the electrodes in volts

i = current passing the discharge in milliamperes.

c – rate of combustion of electrolytic gas in cubic centimetres at NTP per minute

Table I —Copper Electrodes, $p = 45$

$d = 1$ 8			$d = 3$ 8			$d = 7$ 5			$d = 15{\cdot}0$		
v	i	c	v	i	c	v	i	c	v	i	c.
638	0 90	0 35	600	1 07	0 40	658	1 00	0 42	762	0 96	0 38
519	1 45	0 53	545	1 10	0 37	650	1 00	0 38	752	1 00	0 32
510	1 81	0 70	538	1 22	0 42	615	1 12	0 50	732	1 12	0 42
510	2 75	1 10	534	1 26	0 40	608	1 25	0 50	724	1 30	0 49
507	2 72	1 02	526	1 78	0 67	610	1 32	0 51	728	1 36	0 51
505	3 02	1 22	530	2 27	0 85	608	1 50	0 57	726	1 60	0 97
510	3 30	1 45	530	2 45	1 10	608	2 05	1 02	725	1 80	1 15
510	3 47	1 60	528	2 55	1 07	610	2 20	1 17	725	1 88	1 38
508	3 57	1 62	526	3 15	1 70	605	2 20	1 30	725	2·25	2 12
508	3 95	1 93	530	3 55	2 00	610	2 52	1 67	725	2 32	2 07
510	4 39	2 27	525	3 60	2 15	602	2 62	1 75	726	3 16	3 98
510	4 45	2 32	532	4 74	3 17	608	3 22	2 37	722	3 55	4 22
515	5 20	3 05	528	5 67	4 10	608	3 55	2 87			
508	5 20	3 00	525	5 85	4 36	605	3 62	2 87			
506	5 57	3 17	532	5 92	4 17	602	4 30	4 05			
505	6·12	3 70				602	4 60	4·03			
505	6 12	3 59				605	4 92	4 52			
512	7 10	4 32				600	5 02	4 48			
513	7 27	4 75				602	5 10	4 47			

Table II.—Copper Electrodes, $p = 75$.

$d = 1$ 8.			$d = 3$ 8			$d = 7$ 5			$d = 15$ 0		
v	i	c	v	i	c	v	i	c	v	i	c
538	1 39	0 50	638	0 90	0 37	788	0 80	0 32	930	0 93	0 62
532	1 72	0 60	622	1 05	0 37	720	1 00	0 37	938	0 97	0 80
535	2 55	1 00	575	1 17	0 42	710	1 26	0 39	922	1 30	1 45
534	2 75	1 10	574	1 87	0 75	720	1 27	0 49	925	1 38	1 60
532	3 14	1 60	565	2 20	0 90	725	1 77	1 12	910	1 75	3 05
538	3 27	1 60	575	2 35	1 10	718	1 87	1 10	910	1 93	3 30
538	3 40	1 72	580	2 77	1 60	722	1 92	1 14	904	2 05	5 00
536	3 75	2 00	570	2 85	1 60	720	2 56	2 12			
538	4 12	2 45	572	3 20	2 12	718	2 70	2 30		>2 2	Explosion
530	4 25	2 51	573	3 35	2 15	720	3 12	2 85			
540	4 90	3 00	575	5 20	4 37	722	3 25	3 00			
528	5 08	3 15	576	5 38	4 50	710	3 66	3 75			
526	5 25	3 30	574	5 85	4 77	712	3 77	3 77			
						714	4 15	4 98			
525	5 75	3 88				708	4 42	5 34			
538	5 85	3 75									
532	6 90	4 62					>4 5	Explosion			
538	7 05	5 10									

Table III —Copper Electrodes, $p = 90$

$d = 1$ 8			$d = 3$ 8			$d = 7$ 5			$d = 15$ 0		
v	i	c	v	i	c	v	i	c	v	i	c
565	1 25	0 48	648	0 87	0 37	830	0 85	0 35			
560	1 37	0 51	632	0 95	0 35	815	1 02	0 39			
550	1 60	0 61	602	1 12	0 45	812	1 30	0 73			
550	1 82	0 72	608	1 50	0 57	805	1 44	0 94			
555	2 05	0 82	588	1 87	0 90	802	2 01	1 80			
550	2 47	1 05	590	2 05	1 05	790	2 10	1 80			
550	2·52	1 15	600	2 12	1 12	796	2 31	2 30			
545	3 07	1 70	590	2 67	1 70	786	2 87	3 15			
548	3 30	1 82	588	2 90	1 90	785	2 96	4 12			
555	3 60	2 12	588	2 94	2 12						
548	3 95	2 38	586	3 20	2 27		>3	Explosion			
552	4 05	2 38	582	4 30	3 60						
550	4 70	3 00	574	4 37	3 55						
552	4 95	3 30	575	5 20	5 37						
550	5 80	3 45	574	5 20	5 50						
545	5 70	4 07									
547	5 87	3 98		>5 3	Explosion						
550	6 60	5 27									
545	6·96	5 52									

Table IV —Platinum Electrodes, $p = 45$

$d = 1\ 8$			$d = 3\ 8$			$d = 7\ 5$			$d = 15\ 0$		
v	i	c	v	i	c	v	i	c	v	i	c
542	0 87	0 47	662	0 80	0 47	580	1 26	0 70	765	0 73	0 39
488	1 30	0 76	564	0 99	0 55	580	1 47	0 85	755	1 03	0 87
488	1 41	0 80	538	1 22	0 72	580	1 95	1 14	750	1 45	1 72
486	1 82	1 00	535	1 35	0 80	576	2 35	1 37	745	1 70	2 17
488	2 10	1 20	530	1 86	1 07	575	2 85	1 92	738	1 72	2 45
485	2 97	1 75	535	2 14	1 27	575	3 75	3 25	736	2 10	2 95
480	3 00	1 70	532	2 20	1 22	574	3 90	3 30	738	2 12	3 30
480	3 42	1 92	528	2 82	1 62	572	4 42	4 17	730	2 25	3 17
476	3 60	2 10	530	2 20	2 00				732	2 30	3 37
475	3 92	2 43	520	2 35	2 15				735	2 35	4 25
468	4 64	3 07	520	4 50	3 48				730	2 57	4 52
475	4 70	3 12	514	5 10	4 07						
472	4 75	3 33	516	5 17	4 22					> 2 7	Explosion
465	5 37	3 91									
464	5 50	3 89									
462	5 95	4 45									
462	6 27	4 75									
462	6 30	4 90									

Table V —Platinum Electrodes, $p = 75$.

$d = 1\ 8$			$d = 3\ 8$			$d = 7\ 5$			$d = 15\ 0$		
v	i	c	v	i	c	v	i	c	v	i	c
780	0 88	0 50	612	1 12	0 67	920	0 85	0 45	—	0 97	1 00
760	0 95	0 50	605	1 25	0 72	778	1 37	0 75	—	1 12	1 02
725	1 08	0 60	602	1 65	0 95	780	1 77	1 02	—	1 35	2 50
662	1 33	0 72	598	1 96	1 14	750	2 30	1 70	—	1 40	2 14
630	1 55	0 88	590	3 39	2 57	760	3 43	3 62	—	1 56	2 93
562	2 00	1 20	581	3 40	2 68	755	3 80	4 68			
502	2 80	1 70	575	4 89	4 45					>1 7	Explosion
500	3 00	1 74	565	5 52	5 35						
490	3 33	2 19	562	5 65	5 38		>4 0	Explosion			
495	3 45	2 20									
492	3 75	2 53									
490	4 45	3 43									
492	4 57	3 52									
485	4 56	3 41									
488	4 72	3 60									
488	5 35	4 26									
482	5 40	4 40									

Table VI.—Platinum Electrodes, $p = 90$

$d = 1\ 8$			$d = 3\ 8$			$d = 7\ 5$		
v	i	c	v	i	c	v	i	c
935	0 85	0 45	650	1 10	0 70		0 77	0 45
898	0 88	0 48	630	1 35	0 76	—	1 05	0 52
880	1 05	0 62	638	1 61	0 88	—	1 20	0 70
762	1 38	0 80	625	1 92	1 20	870	1 53	1 21
615	1 95	1 10	625	1 98	1 37	865	1 73	1 52
612	2 12	1 25	620	3 12	2 90	854	2 00	2 05
578	2 52	1 55	612	3 30	3 10	831	2 70	4 32
545	2 75	1 92	600	4 00	4 87			
526	3 27	2 37	602	4 32	6 07		>2 8	Explosion
530	3 37	2 52						
530	3 75	2 98		>4 4	Explosion			
535	4 28	3 70						
526	4 58	3 85						
523	4 60	3 88						
528	4 85	4 72						
525	5 10	5 02						
524	5 20	6 15						
	>5 3	Explosion						

Explanation and Notation of the Graphs (figs 6, 7, 8 and 9)

Two sets of graphs are shown in each of the four diagrams (figs 6, 7, 8 and 9) incorporating the experimental results obtained at pressures of 30 mm and 60 mm, which have not been included in the above tables The upper set, drawn in dot-dash lines, shows the characteristic curves of the discharge for each degree of separation of the electrodes, in millimetres, d, which were obtained by plotting the potential fall between the electrodes in volts, v, against the current passing the discharge in milliamperes, i The lower set, drawn in full lines, contains the curves connecting the rate of combustion in cubic centimetres at NTP per minute, c, with the current in milliamperes, i In both sets of graphs, points of the curves corresponding to the different degrees of separation of the electrodes employed are marked distinctively thus —

○ indicates results obtained with $d = 1{\cdot}8$ mm
ϕ „ „ „ „ $d = 3\ 8$ mm
× „ „ „ „ $d = 7\ 5$ mm
● „ „ „ „ $d = 15\ 0$ mm

Discussion of the Results

A noteworthy feature of the rate of combustion current (c/i) curves is that, prior to following independent courses, they coincide and form the straight, line AB. Thus the curve AHK ($d = 15·0$ mm.) consists of two distinct sections, one of which AH, in coinciding with AB, is common to the remaining curves, the other section, HK, being independent. It will be convenient, for the purposes of discussion, to consider the coinciding and independent sections of the curves separately.

A. *The Coinciding Sections of the c/i Curves.*—At all points on the straight line, AB, formed by the coinciding sections of the c/i curves, *the rate of combustion is directly proportional to the current.* Produced, AB passes through, or nearly through, zero. The mean values of the ratio c/i at various pressures, for all points on AB are tabulated below.

Table VII.

p	Copper Electrodes	Platinum Electrodes
	c/i	c/i
30	0·40	0·58
45	0·39	0·58
60	0·39	0·59
75	0·39	0·58
90	0·39	0·59

Thus, for all points on AB, the ratio of the rate of combustion to current is a constant, the value of which depends solely on the nature of the electrode material and is independent of (a) the gas pressure, (b) the degree of separation of the electrodes, and (c) the potential fall between the electrodes. In describing the appearance of the discharge, it has already been remarked that, provided the same current be maintained, variation in the degree of separation of the electrodes results only in a change in the size of the brush-shaped glow (positive column) of the inter-electrode zone. Thus from these facts the conclusion may be drawn that, for all points on AB, *combustion of the electrolytic gas occurred only in either one or both of the electrode zones, and not in the inter-electrode zone.* The answer to the further question as to where the combination had occurred was furnished by two further series of experiments, in the first of which a copper cathode and platinum anode and, in the second, a platinum cathode and copper anode were employed. The results are recorded graphically in fig. 10.

The value of the ratio c/i over AB (Cu cathode, Pt anode) is now found to be 0·40, and 0·56 over A′B′ (Pt cathode, Cu anode). The former value is slightly higher than the mean of those previously recorded for copper, the latter slightly lower than that for platinum electrodes It therefore follow that for all points on AB *combustion was almost wholly confined to the cathod*

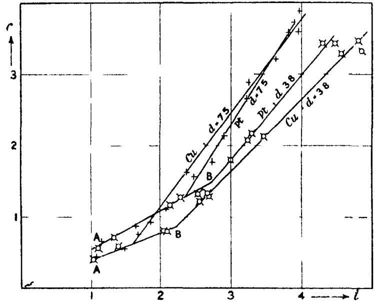

Fig 10

zone The rate of combination of the electrolytic gas was therefore proportional to the number of ions arriving at the cathode in a given time

In view of the fact that the value of c/i is higher for a platinum than for a copper cathode it might at first sight appear that the combination taking place in the vicinity of the cathode is largely catalytic combustion thus occurring on or in the surface of the metal However the fact that c/i is independent of variations in pressure from 30 mm to 90 mm invalidates any such explanation

Further evidence to this effect was furnished by a series of experiments in which a platinum platinum rhodium thermocouple was employed as cathode thus enabling the variation of temperature of the cathode zone with current to be determined The wires (No 26 S W G) of the couple were fused together in an oxy hydrogen flame The junction was filed and polished to a cone of the same shape and dimensions as that of the normal electrodes hitherto employed the whole of the actual junction being inside the cone itself The

T 2

thermocouple galvanometer was set up on the table on a block of paraffin wax The negative lead of the high-tension circuit was connected to one wire of the couple With currents of not less than 0 8 milliampere passing the discharge, the cathode glow entirely surrounded the junction The results of these experiments showed that, within the range of pressure, electrode separation and current examined by us, the mean temperature of the cathode zone is practically independent of the pressure and extent of separation of the electrodes, and is proportional to the current, rising from 20° C with zero current to 530° with 6 milliamperes, the rate of increase of temperature being 85° per one milliampere increase in current, and very nearly uniform Prof Bone informs us that, some time ago, he found that between 350° and 400° the temperature coefficient of the catalytic combustion of electrolytic gas in contact with silver wire was 1 4 for each 10° rise in temperature It may therefore be concluded that the combustion which took place at the cathode in our said experiments was non catalytic, and that some other explanation must be forthcoming for the observed variation in the value of the ratio c/i with the nature of the cathode material A comparison of the characteristic curves of the discharge between copper or platinum for the smallest degree of separation of the electrodes employed suggests that the cathode fall of potential of copper (coated with oxide) in steam is probably higher than that of platinum From this it may be inferred that, under the conditions of our experiments, electrons are emitted more readily by platinum than by copper Whether or not the true explanation of the foregoing relationship lies in this direction is not yet clear In order to elucidate the matter further, however, we are now carrying out experiments with electrodes of more electropositive metals than either of the two so far employed

B *The Independent Sections of the c/i Curves* —An inspection of the diagrams (figs 6 to 10) shows that the independent sections of the c/i curves are straight lines, though the steeper curves, on exceeding a certain current, merge into true curves which rise rapidly towards the ignition point

The independent sections of the c/i curves leave AB at the currents tabulated below, which may for convenience be termed " independence currents "

It will be seen from Table VIII that, except in the case of the greatest degree of separation of the electrodes, the independence currents are less for copper than for platinum, and that the nature of the anode material has little or no effect upon the value of these currents Furthermore, an increase either in pressure or degree of separation of the electrodes results in a decrease of the independence current From these facts it may be concluded that,

Table VIII

p	d − 1 8		d − 3 8		d ▴ 7 5		l 15 0	
	Cu +	Pt	Cu +	Pt	Cu	Pt +	Cu +	Pt +
30	2 90	3 44	2 43	3 10	1 83	2 76	1 54	0 83
45	2 82	3 52	2 30	2 94	1 75	2 57	1 40	0 84
60	2 70	3 18	2 22	2 75	1 62	2 33	1 15	0 65
75	2 54	2 90	2 00	2 40	1 40	1 95	0 75	0 76(?)
90	2 23	2 30	1 70	1 75	1 07	1 25	—	—
	Cu+ Pt		Cu+ Pt		Cu+ Pt			
60	3 30		2 70		2 35			
	Pt+ Cu		Pt+ Cu		Pt+ Cu			
60	2 65		2 20		1 70			

for the independent sections of the c/i curves combustion of the electrolytic gas is no longer confined to the cathode zone but also occurs in the inter electrode zone the anode zone, however still remaining to all intents and purposes, inactive The combustion taking place in the inter electrode zone is probably confined to the only luminous portion thereof, namely, the positive column It may therefore be inferred that of the total combustion taking place as represented by the independent sections of the c/i curves the amount of chemical action occurring in the positive column is the difference between the total chemical action and that taking place at the cathode If for convenience, the ratio of rate of combustion to current for each independent section is referred to co ordinates parallel to those hitherto employed, but passing through that point on AB at which each section becomes independent, and from the value of the ratio thus obtained that of the ratio c/i for AB is subtracted, we obtain c/i' which is the ratio of the rate of that combustion which occurred in the positive column to current The values of c/i' are tabulated below

Table IX brings out the following salient features of the independent sections of the c/i curves —(i) The nature of the electrode material has, on the whole, little or no effect upon the value of c'/i', for platinum the value of this ratio is, as a rule, though not always, a little greater than for copper The difference is, however, in most cases slight and within the limits of experimental error (ii) The value of c'/i' increases with increasing pressure, and also (iii) with increasing degree of separation of the electrodes These facts constitute further proof that the chemical activity represented by c'/i' is practically confined to the inter-electrode zone, and, in all probability, to the positive column of the discharge

Table IX

p	$d = 1\ 8$		$d = 3\ 8$		$d = 7\ 5$		$d = 15\ 0$	
	Cu_-^+	Pt_-^+	Cu_-^+	Pt_-^+	Cu_-^+	Pt_-^+	Cu_-^+	Pt_-^+
30	0 35	0 36	0 47	0 53	0 83	0 72	1 14	1 12
45	0 39	0 40	0 53	0 55	0 80	0 85	1 39	1 47
60	0 42	0 46	0 55	0 63	0 91	1 11	1 48	1 23
75	0 46	0 46	0 68	0 67	0 99	1 08	1 89	—
90	0 46	0 57	0 71	0 76	1 09	1 22	—	—

The abrupt nature of the departure from AB of the independent sections of the c/i curves remains to be accounted for A detailed spectroscopic examination of the discharge is now under way, and will, it is hoped, furnish a satisfactory explanation of this phenomenon We believe at the moment that the inactivity or otherwise of the positive column may possibly depend upon the nature of the ionisation of the gases through which it passes

Reference has already been made to the fact that the steeper independent sections of the c/i curves begin to rise rapidly when a certain current is exceeded Had a more powerful source of current been available in the course of these experiments, there is no doubt that a similar rapid curving upwards at some point or other on all the curves would have been found In several cases (*see* Tables II to VI and the diagrams in figs 7 to 9) currents in excess of those at which a steepening up of the curves occurred were employed with the object of attempting to determine the lowest pressures at which such currents were capable of igniting the gaseous mixtures With the experimental procedure adopted, by which the electrolytic gas was admitted into the combustion chamber after the discharge had been started, it was found that the pressure at which ignition with a given current occurred increased with the rate of admission of the gas If the gas were rapidly admitted to a suitable pressure, and this pressure then maintained as closely as possible by balancing the rate of slow combustion by regulation of the rate of supply of electrolytic gas, it was found that a definite interval of time elapsed before ignition occurred This interval, or lag, which in some cases amounted to several seconds, increased with decrease in either the current or pressure of the gas

In the light of the foregoing facts and considerations, the following suggestions may be advanced as a possible explanation of the mechanism of electrical ignition of explosive gaseous media —

When an electric discharge, powerful enough to bring about ignition, is passed through such a medium, chemical combination occurs in both the cathode and inter-electrode zones The rate of such combination is directly proportional to the current, that in the cathode zone being proportional to the total number of ions arriving in unit time at the cathode, and that occurring in the inter-electrode zone (positive column) being probably proportional to the number of suitable ions formed by the passage of the current The heat liberated by the gases on combination contributes to the number of ions formed by the passage of the current With an igniting current, this heat source of ionisation produces ions more rapidly than they recombine to electrically neutral atoms or molecules, or are removed from the zone of the discharge by convection currents in the gas Thus this source of ionisation is cumulative and leads to ignition and explosion when a sufficient concentration of suitable ions has been attained Furthermore, ignition does not occur at the actual moment of initial passage of the igniting current, but only after the lapse of a definite interval, or lag, during which that concentration of suitable ions which is necessary to bring about ignition is gradually attained by the cumulative addition of those ions which are formed by the heat of combination of the combustible gases, to the ions due to the passage of the current Inspection of the diagrams (figs 6 to 7) shows that whether this critical ignition concentration of ions is first attained in the cathode or inter-electrode zone, or in both simultaneously, depends in the main upon the degree of separation of the electrodes, and to a lesser extent upon the pressure of the gas and the nature of the material of the cathode The lag found by us in attempting to determine the least igniting currents under various conditions, and the lack of agreement in the results obtained, which was certainly due to lag effects, are, at the same time, accounted for on a basis of this hypothesis, according to which heat plays no rôle beyond that of furnishing ions

Summary and Concluding Remarks

In the foregoing experiments it has been shown that --

(i) An electric discharge can be passed through electrolytic gas in such a manner that combustion takes place at a rate which is determined only by the current passed by the discharge

(ii) Up to a certain limiting current which depends upon (1) the nature of the cathode, (2) the gas pressure, and (3) the degree of separation of the electrodes, combustion is confined to the cathode zone

(iii) Such cathodic combustion is independent of (1) the potential fall between, and the degree of separation of, the electrodes, (2) the gas pressure, and (3) the temperature of the discharge, but depends upon the nature of the cathode material

(iv) The rate of such cathodic combustion is directly proportional to the current, *i e*, to the number of ions arriving at the cathode in a given time

(v) After a certain limiting current has been exceeded, combustion commences *abruptly* in the inter-electrode zone and is thereafter superposed upon the aforesaid cathodic combustion, the two then continuing as independent simultaneous effects

(vi) The said inter-electrodic combustion is itself, like the cathodic, also proportional to the current passing, unlike the cathodic, however, it is independent of the material of the electrodes, but dependent upon (1) the gas pressure and (2) the degree of separation of the electrodes

(vii) Little or no combustion takes place in the anode zone

From these facts it may be concluded that the combustion which occurred under the said conditions was primarily determined by the ionisation of the gaseous medium through which the current passed.

The abrupt superposition of the inter-electrodic upon the cathodic combustion is strongly suggestive of a quantum effect Thus it may be that whereas in the cathodic zone, in which the potential fall is undoubtedly very steep, the ionisation of the gases is from the outset of a character favourable to combustion, in the inter-electrode zone, where the potential fall is much less steep, only one or neither of the constituents of the gaseous medium is suitably ionised until a certain limiting potential fall is attained At any rate, in view of the results obtained, it is difficult to resist the conclusion that both cathodic and inter-electrodic combustion are determined by ionisation.

It is proposed to extend this investigation to other cases of gaseous combustion and to supplement these experiments with spectroscopic observations, in correlation with other investigations upon gaseous combustion proceeding in this Department of the Imperial College

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The Elimination of the Nodes in Quantum Mechanics

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§ 1 *Introduction*

The laws of classical mechanics must be generalised when applied to atomic systems, the generalisation being that the commutative law of multiplication, as applied to dynamical variables, is to be replaced by certain quantum conditions, which are just sufficient to enable one to evaluate $xy - yx$ when x and y are given It follows that the dynamical variables cannot be ordinary numbers expressible in the decimal notation (which numbers will be called c-numbers), but may be considered to be numbers of a special kind (which will be called q-numbers), whose nature cannot be exactly specified, but which can be used in the algebraic solution of a dynamical problem in a manner closely analogous to the way the corresponding classical variables are used *

The only justification for the names given to dynamical variables lies in the analogy to the classical theory, *e g* , if one says that x, y, z are the Cartesian co-ordinates of an electron, one means only that x, y, z are q-numbers which appear in the quantum solution of the problem in an analogous way to the Cartesian co-ordinates of the electron in the classical solution It may happen that two or more q-numbers are analogous to the same classical quantity (the analogy being of course, imperfect and in different respects for the different q numbers), and thus have claims to the same name This occurs, for instance, when one considers what q-numbers shall be called the frequencies of a multiply periodic system, there being orbital frequencies and transition frequencies, either of which correspond in certain respects to the classical frequencies In such a case one must decide which of the properties of the classical variable are dynamically the most important, and must choose the q-number which has these properties to be the corresponding quantum variable

In the classical treatment of the dynamical problem of a number of particles or electrons moving in a central field of force and disturbing one another, one always begins by making the initial simplification, known as the elimination of the nodes, which consists in obtaining a contact transformation from the

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* 'Roy Soc Proc ,' A, vol. 110, p 561 (1926) The method there given in §§ 1–4 is the one used here

Cartesian co-ordinates and momenta of the electrons to a set of canonical variables, of which all except three are independent of the orientation of the system as a whole, while these three determine the orientation. In the absence of an external field of force, the Hamiltonian, when expressed in terms of the new variables, must be independent of these three, which simplifies the equations of motion It can be shown that the new variables may be taken to be the following the distance r of each electron from the centre, with the radial component of momentum p_r as conjugate variable, the component M_z ($= p$ say) of the total angular momentum of the system in a given direction, z say, with the azimuth about this direction of the direction of total momentum as conjugate variable, and in the case of a system with a single electron the only other new variables may be taken to be the magnitude of the angular momentum k, with the angle θ in the orbital plane between the radius vector and the line of intersection of the orbital plane with the plane xy as conjugate variable, while in the case of two electrons the remaining new variables may be taken to be the angular momenta k and k' of the two electrons, with, for conjugate variables, the angles θ and θ' between the radius vectors and the line of nodes, and the total angular momentum j with the azimuth ψ of the line of nodes about the direction of j for conjugate variable The transformation does not involve anything essentially different when there are more than two electrons, as we may consider all the electrons except one as forming an inner system or core which plays the part of the second electron when there are only two, so that the j of the core counts as the k' of the whole system, the ψ of the core counts as the θ' of the whole system, while the magnitude of the resultant of k and k' is the j of the whole system, and the azimuth about the direction of this resultant of the line of intersection of planes perpendicular to the vectors of k and k' is the ψ All the new variables are independent of the orientation of the system as a whole except p, ϕ and ψ (or θ when there is only one electron) The variables k, k', j and p may be called action variables, and their canonical conjugates angle variables

The object of the present paper is to perform the corresponding initial simplification in the quantum treatment of the problem by the introduction of certain quantum variables, which will be given the same names r, p_r, k, θ, etc, whose properties upon investigation will be found to be closely analogous to those of the classical variables. The quantum variables, of course, cannot be considered geometrically The geometrical relations satisfied by the classical variables must be expressed in an analytic form, so that one can then try to obtain quantum variables which satisfy the same algebraic relations If a classical variable is independent of the orientation of the system as a whole, the corresponding quantum variable must be invariant under the transformation

$$\left.\begin{array}{ll} \bar{x} = l_1 x + m_1 y + n_1 z & \bar{p}_x = l_1 p_x + m_1 p_y + n_1 p_z \\ \bar{y} = l_2 x + m_2 y + n_2 z & \bar{p}_y = l_2 p_x + m_2 p_y + n_2 p_z \\ \bar{z} = l_3 x + m_3 y + n_3 z & \bar{p}_z = l_3 p_x + m_3 p_y + n_3 p_z \end{array}\right\}, \qquad (1)$$

where the l's, m's and n's are c-numbers satisfying the same relations as the classical coefficients for a rotation of axes The new variables, of course must all be real, and also the angle variables θ, θ', ψ and ϕ must be such that the Cartesian co-ordinates, when expressed in terms of the new variables, are multiply periodic in the θ, θ', ψ and ϕ of period 2π Finally, the most essential property of the new variables is that they shall be canonical, which can be verified only by evaluating all their P B 's (Poisson bracket expressions) taken two at a time

In the present paper we are not concerned very much with what the Hamiltonian of the system is We simply want to find a contact transformation from the Cartesian co ordinates and momenta to the new variables, namely, the r's, p_r's and certain variables which we call action and angle variables These can be true action and angle variables only if the Hamiltonian is a function of the r's, p_r's and action variables only In this case, to complete the solution of the dynamical problem, it is necessary only to obtain a contact transformation from the r's and p_r's to extra action and angle variables, which transformation may require the addition of functions of the r's and p_r's to the previous angle variables When the Hamiltonian does not satisfy this condition, the action and angle variables introduced in the present paper form a preliminary system of canonical variables, from which the final uniformising variables may be obtained by a further contact transformation It can be shown that the kinetic energy of an electron is a function of the r, p_r and action variables only, and hence, if the total field in which the electron moves is approximately central or symmetrical about the z-axis, the Hamiltonian will differ from a function of the r's, p_r's and action variables only, only by a small quantity, so that the further contact transformation can be made with the help of perturbation theory In the absence of an external field of force the Hamiltonian must in any case be a function only of those of the new variables that are invariant under the transformation (1), since the Hamiltonian itself is invariant under this transformation

§ 2 *Preliminary Algebraic Relations*

Let x, y, z and p_x, p_y, p_z be the Cartesian co-ordinates and momenta of an electron. Any function of the co-ordinates and momenta of one electron commutes with any function of those of another. Define r and p_r by

$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}}, \tag{2}$$

$$rp_r = xp_x + yp_y + zp_z - ih \tag{3}$$

Then we have, since r commutes with x, y and z

$$[r, rp_r] = x\,[r, p_x] + y\,[r, p_y] + z\,[r, p_z]$$

Now

$$[r, p_x] = [(x^2 + y^2 + z^2)^{\frac{1}{2}}, p_x] = x/(x^2 + y^2 + z^2)^{\frac{1}{2}} = x/r,$$

with similar equations for $[r, p_y]$ and $[r, p_z]$. Hence

$$[r, rp_r] = (x^2 + y^2 + z^2)/r = r,$$

or

$$[r, p_r] = 1$$

Thus r and p_r are canonically conjugate and may be taken to be a pair of the new variables, as they are obviously invariant under the transformation (1). The $(-ih)$ is put in equation (3) for symmetry and to make p_r real, the conjugate imaginary equation, obtained by writing $-i$ for i and reversing all orders of factors of products, being

$$p_r r = p_x x + p_y y + p_z z + ih \tag{3'}$$

which agrees with (3).

The components of angular momentum* of an electron are defined, as on the classical theory, by

$$m_x = yp_z - zp_y, \quad m_y = zp_x - xp_z, \quad m_z = xp_y - yp_x$$

We have at once the identity

$$xm_x + ym_y + zm_z = 0 \tag{4}$$

as on the classical theory. Also

$$\left.\begin{aligned} [m_z, x] &= [xp_y - yp_x, x] = y \\ [m_z, y] &= [xp_y - yp_x, y] = -x \end{aligned}\right\}, \tag{5}$$

$$[m_z, z] = [xp_y - yp_x, z] = 0, \tag{6}$$

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[*] The angular momentum relations of this section have been obtained independently by Born, Heisenberg and Jordan ('Zeits f Phys.,' vol 35, p. 557 (1926))

and similarly

$$[m_z, p_x] = p_y, \quad [m_z, p_y] = -p_x, \tag{7}$$

$$[m_z, p_z] = 0, \tag{8}$$

with corresponding relations for m_x and m_y Further,

$$\left.\begin{aligned} [m_x, m_y] &= [m_x, zp_x - xp_z] = [m_x, z]\, p_x - x\,[m_x, p_z] \\ &= -yp_x + xp_y = m_z \\ \text{and similarly} \quad [m_y, m_z] &= m_x, \quad [m_z, m_x] = m_y \end{aligned}\right\} \tag{9}$$

These relations will be continually used in the subsequent work Equations (5), (7) and (9) may easily be remembered from the fact that the + sign occurs when the cyclic order ($x\ y\ z\ x$) is preserved, and the − sign occurs with the reverse order

From (2), (5) and (6),

$$[r^2, m_z] = [x^2 + y^2, m_z] = -2xy + 2xy = 0,$$

and from (3), (5), (6), (7) and (8),

$$[rp_r, m_z] = [xp_x + yp_y, m_z] = -yp_x - xp_y + xp_y + yp_x = 0$$

so that r and p_r commute with m_z, and therefore from symmetry also with m_x and m_y, and therefore with any function of the angular momenta

Put

$$M_x = \Sigma m_x \quad M_y = \Sigma m_y \quad M_z = \Sigma m_z,$$

the summation being extended over all the electrons We have at once from (5) and (6) for each electron

$$[M_z, x] = y, \quad [M_z, y] = -x, \quad [M_z, z] = 0 \tag{10}$$

Also

$$\left.\begin{aligned} [M_x, M_y] &= [\Sigma m_x, \Sigma m_y] = \Sigma\,[m_x, m_y] = \Sigma m_z = M_z \\ \text{and similarly} \quad [M_y, M_z] &= M_x, \quad [M_z, M_x] = M_y \end{aligned}\right\} \tag{11}$$

Let

$$m_x^2 + m_y^2 + m_z^2 = m^2$$

We have from (9),

$$[m^2, m_z] = [m_x^2 + m_y^2, m_z] = -m_y\, m_x - m_x\, m_y + m_x\, m_y + m_y\, m_x = 0,$$

so m commutes with m_z, and hence also with m_x and m_y Similarly if

$$M_x^2 + M_y^2 + M_z^2 = M^2$$

M commutes with M_x, M_y and M_z

The kinetic energy of an electron is a function of $(p_x^2 + p_y^2 + p_z^2)$ With the help of (2), (3) and (3′) we obtain

$$\begin{aligned} m^2 &= \Sigma_{xyz} (yp_z - zp_y)^2 = \Sigma_{xyz} (yp_z yp_z + zp_y zp_y - yp_z zp_y - zp_y yp_z) \\ &= \Sigma_{xyz} (y^2 p_z^2 + z^2 p_y^2 - yp_y p_z z - zp_z p_y y - xp_x p_x x + x^2 p_x^2 - 2ihxp_x) \\ &= (x^2+y^2+z^2)(p_x^2+p_y^2+p_z^2) - (xp_x+yp_y+zp_z)(p_x x+p_y y+p_z z+2ih) \\ &= r^2 (p_x^2+p_y^2+p_z^2) - (rp_r + ih)(p_r r + ih) \\ &= r^2 (p_x^2+p_y^2+p_z^2) - r^2 p_r^2 \end{aligned}$$

Hence

$$p_x^2 + p_y^2 + p_z^2 = p_r^2 + m^2/r^2 \tag{12}$$

as on the classical theory Now m^2 is going to be a function of the action variables, and hence the kinetic energy of the system will be a function of the r's, p_r's and action variables

We shall not be concerned further with the r's and p_r's except to verify that they commute with each of the action and angle variables that will be introduced, this being necessary for the variables to be canonical

§ 3 *The Action Variables*

On the classical theory one of the action variables to be introduced, namely, k, is just equal to m The quantum variable k may not be equal to m, but must be chosen such that x, y and z are periodic functions of its canonically conjugate variable θ of period 2π On the classical theory, if a co-ordinate, z say, is expanded as a Fourier series in the angle variables, the coefficients of the terms involving $e^{ni\theta}$ all vanish unless $n = \pm 1$ This fact is expressible analytically by the equation $\partial^2 z/\partial\theta^2 = -z$, or in P B 's by $[k, [k, z]] = -z$ We try to choose our quantum variable k so as also to satisfy

$$[k, [k, z]] = -z \tag{13}$$

This relation would ensure that when z is expressed in terms of the new variables, it would be periodic in θ of period 2π, and, further, that all the coefficients in the Fourier expansion would vanish except those of $e^{i\theta}$ and $e^{-i\theta}$ terms The ordinary selection rule for k would then follow

Equation (13) gives

$$[k^2, [k, z]] = k [k, [k, z]] + [k, [k, z]] k = -(kz + zk),$$

and hence

$$\begin{aligned}[k^2, [k^2, z]] &= k\,[k^2, [k, z]] + [k^2, [k, z]]\,k = -(k^2 z + 2kzk + zk^2) \\ &= -2\,(k^2 z + zk^2) + (k^2 z - 2kzk + zk^2) \\ &= -2\,(k^2 z + zk^2) - h^2\,[k, [k, z]] \\ &= -2\,(k^2 z + zk^2) + h^2 z\end{aligned}$$

or

$$\tfrac{1}{2}[k^2, [k^2, z]] = -(k^2 - \tfrac{1}{4}h^2)\,z - z\,(k^2 - \tfrac{1}{4}h^2) \tag{14}$$

Now from (5) and (6)

$$\begin{aligned}\tfrac{1}{2}\,[m^2, z] &= \tfrac{1}{2}\,[m_x^2 + m_y^2, z] = \tfrac{1}{2}\,(-ym_x - m_x y + xm_y + m_y x) \\ &= m_y x - m_x y + ihz = m_y x - ym_x = xm_y - m_x y\end{aligned} \tag{15}$$

Similar relations hold for $\frac{1}{2}\,[m^2, x]$ and $\frac{1}{2}\,[m^2, y]$ Hence

$$\begin{aligned}\tfrac{1}{2}[m^2, [m^2, z]] &= m_y\,[m^2, x] - m_x\,[m^2, y] + ih\,[m^2, z] \\ &= m_y 2\,(ym_z - m_y z) - m_x 2\,(m_x z - xm_z) + ih\,[m^2, z] \\ &= 2\,(m_x x + m_y y + m_z z)\,m_z - 2\,(m_x^2 + m_y^2 + m_z^2)\,z + ih\,[m^2, z] \\ &= -2m^2 z + (m^2 z - zm^2) \\ &= -m^2 z - zm^2\end{aligned} \tag{16}$$

Comparing this with equation (14) we see that they agree if we take

$$m^2 = k^2 - \tfrac{1}{4}h^2 = k_1 k_2, \tag{17}$$

where

$$k_1 = k + \tfrac{1}{2}h, \qquad k_2 = k - \tfrac{1}{2}h$$

(In general we shall take the suffix 1 attached to any action variable to denote the value of that variable increased by $\frac{1}{2}h$, and the suffix 2 to denote its value reduced by $\frac{1}{2}h$)

With k defined by (17), equation (14) follows from equation (16), but equation (13) does not necessarily then follow from equation (14) We may, however, take (13), together with the corresponding equations

$$[k, [k, x]] = -x \qquad [k, [k, y]] = -y \tag{18}$$

as completing the definition of k, which had previously been defined only through k^2 It seems probable that in general an algebraic equation in quantum algebra has an infinite number of roots, *e g* , the algebraic equation $xa - ax = b$ is analogous to a differential equation on the classical theory, and its general solution contains arbitrary c numbers It thus appears to be reasonable for one to take two or more equations to define a q-number when necessary, provided these equations are consistent, as in the present case

One may examine the necessity for the further assumptions (13), (18) in the definition of k by the matrix method used by Born, Heisenberg and Jordan * If one regards (14) as a matrix equation and equates the (nm) components of either side, one obtains a relation effectively the same as Born, Heisenberg and Jordan's equation 22 Kap 4 (except for the fact that Born, Heisenberg and Jordan are using M instead of m, and X, a linear function of x, y and z, instead of z) From this these authors deduce that all X (nm) components vanish except those related to two k's, a_n and a_m say, that satisfy

$$a_n = \pm a_m \pm 1 \qquad \text{(23) Kap 4}$$

But we want each X (nm) to vanish except when

$$a_n = a_m \pm 1 \qquad \text{(23') Kap 4.}$$

Born, Heisenberg and Jordan state that negative values of k can be ignored without loss of generality, but this is justifiable only if it can be shown that transitions from a positive to a negative k cannot occur This cannot be done without further assumption, since if there is a matrix representation for which every X (nm) vanishes except when (23') Kap 4 is satisfied, one can obtain from it others for which this condition is not fulfilled, but only the condition that each X (nm) vanishes except when (23) Kap 4 is satisfied, by interchanging in the matrix k some of the pairs of rows, and the corresponding pairs of columns, for which the a_n's are equal in magnitude but opposite in sign, as this process does not affect the validity of any matrix equation that involves k only through k^2 Equations (13), (18) supply the necessary further assumption.

One can take as another action variable the quantity M_z, equal to p say, since from (10)

$$\left.\begin{array}{l}[p, [p, x]] = \quad [p, y] = -x \\ {[p, [p, y]] = -[p, x] = -y}\end{array}\right\} \qquad (19)$$

These equations show that x and y are periodic functions of ϕ, the variable conjugate to p, of period 2π, and that all the coefficients in their Fourier expansions vanish except those of $e^{i\phi}$ and $e^{-i\phi}$ terms Further, since $[p, z] = 0$, all the coefficients in the Fourier expansion of z vanish except those of terms independent of ϕ The selection rules for p follow from this

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* Born, Heisenberg and Jordan, *loc cit*

Again, when there is more than one electron in the system, we can define j by

$$M^2 = j^2 - \tfrac{1}{4}h^2 = j_1, j_2, \tag{20}$$

analogous to (17), and take j as an action variable, because, as we shall show later, quantities μ_x, μ_y, μ_z can be found which satisfy

$$[j, [j, \mu_x]] = -\mu_x, \quad [j, [j, \mu_y]] = -\mu_y, \quad [j, [j, \mu_z]] = -\mu_z \tag{21}$$

From the results of § 2 it is evident that j, p and the k's commute with r and p_r and with one another, and also j and the k's are invariant under the transformation (1)

§ 4 *The Angle Variables*

Each of the angle variables w is given on the classical theory by e^{iw} being equal to the square root of the ratio of two quantities that are conjugate imaginaries, i e by a relation of the type

$$e^{iw} = \left(\frac{a + ib}{a - ib}\right)^{\frac{1}{2}} \tag{22}$$

where a and b are real This, of course, makes w real, since if one writes $-i$ for i in (22) it remains true On the quantum theory there are two corresponding ways by which one could define e^{iw}, namely,

$$e^{iw} = \left\{(a + ib)\frac{1}{a - ib}\right\}^{\frac{1}{2}} \qquad \text{and} \qquad e^{iw} = \left\{\frac{1}{a - ib}(a + ib)\right\}^{\frac{1}{2}},$$

but neither of these makes w real The correct quantum generalisation of (22) is the more symmetrical relation

$$e^{iw}(a - ib)\,e^{iw} = a + ib. \tag{23}$$

This becomes, when one equates the conjugate imaginaries of either side

$$e^{-iw}(a + ib)\,e^{-iw} = a - ib,$$

which is equivalent to (23), so that w defined in this way is real We may solve equation (23) for e^{iw} in either of two ways, namely,

$$e^{iw}(a - ib)\,e^{iw}(a - ib) = (a + ib)(a - ib),$$

giving

$$e^{iw}(a - ib) = \{(a + ib)(a - ib)\}^{\frac{1}{2}} = \{(a + ib)(a - ib)\}^{-\frac{1}{2}}(a + ib)(a - ib),$$

so that

$$e^{iw} = \{(a + ib)(a - ib)\}^{-\frac{1}{2}}(a + ib), \tag{24}$$

or alternatively

$$(a - ib)\,e^{iw}(a - ib)\,e^{iw} = (a - ib)(a + ib),$$

which gives

$$e^{iw} = (a + ib)\{(a - ib)(a + ib)\}^{-\frac{1}{2}} \tag{25}$$

Suppose now that J is an action variable such that

$$[\mathrm{J}, a] = b, \qquad [\mathrm{J}, b] = -a \tag{26}$$

We have

$$[\mathrm{J}, a + ib] = b - ia = -i(a + ib)$$

$$[\mathrm{J}, a - ib] = b + ia = i(a - ib),$$

so that

$$\left.\begin{aligned} \mathrm{J}(a + ib) &= (a + ib)(\mathrm{J} + h) \\ \mathrm{J}(a - ib) &= (a - ib)(\mathrm{J} - h) \end{aligned}\right\}, \tag{27}$$

and

$$\mathrm{J}(a + ib)(a - ib) = (a + ib)(\mathrm{J} + h)(a - ib) = (a + ib)(a - ib)\,\mathrm{J},$$

so that J commutes with the product $(a + ib)(a - ib)$ Hence from (24) or (25)

$$\mathrm{J}e^{iw} = e^{iw}(\mathrm{J} + h),$$

or

$$[e^{iw}, \mathrm{J}] = ie^{iw}$$

It does not follow rigorously that $[w, \mathrm{J}] = 1$, but since w occurs in the analysis only through e^{iw}, the relation $[e^{iw}, \mathrm{J}] = ie^{iw}$ is sufficient to show that we can take w to be the variable conjugate to J

From (26)

$$[\mathrm{J}, [\mathrm{J}, a]] = -a \tag{28}$$

Hence, to determine the angle variable w canonically conjugate to any action variable J, one must look for a quantity a that satisfies (28) and that commutes with each of the other action variables, and then, if it can be found, define w by (23) with b equal to $[\mathrm{J}, a]$ This will make w real and conjugate to J, and will make it commute with the other action variables It would, of course, have to be verified that it commutes with r and p_r (On the classical theory the conditions that a must satisfy are that it must vary periodically according to the cosine law when w increases uniformly and the other new variables are kept constant, and must remain constant when the r's, p_r's, action variables and w are kept constant and the other angle variables vary arbitrarily)

To determine, for instance, the angle variable θ canonically conjugate to the k of § 3, we know that $[k, [k, z]] = -z$ and that z commutes with p, and hence for the case of a system with a single electron when there is no other action variable, we can take θ to be defined by

$$e^{i\theta}(z - i[k, z])\,e^{i\theta} = z + i[k, z]. \tag{29}$$

We shall have to take a different value for a when there is more than one electron in the system, since z does not commute with j It is obvious that θ, defined by (29) or

$$e^{i\theta} = \{(z + i[k, z])(z - i[k, z])\}^{-\frac{1}{2}}(z + i[k, z]),$$

commutes with r since z and k do so. To prove that it also commutes with p_r we have

$$[z, rp_r] = z$$

or

$$z\,(rp_r) = (rp_r + ih)\,z.$$

This equation must still be true when for z is substituted $(z + i\,[k, z])$ or $(z - i\,[k, z])$ or $\{(z + i\,[k, z])\,(z - i\,[k, z])\}^{\frac{1}{2}}$.* It follows that e^{iw} commutes with rp_r and hence with p_r. From (27) we have the equation

$$k_2\,(z + i\,[k, z]) = (z + i\,[k, z])\,k_1 \tag{30}$$

which will be required later.

In the same way we may define ϕ, the angle variable canonically conjugate to p, by taking $a = \mathrm{M}_x$, since we know that $[p, [p, \mathrm{M}_x]] = -\mathrm{M}_x$ and that M_x commutes with each k and with j. We thus have

$$e^{i\phi}(\mathrm{M}_x - i\mathrm{M}_y)\,e^{i\phi} = \mathrm{M}_x + i\mathrm{M}_y.$$

It is obvious that r and p_r commute with ϕ since they commute with M_x and M_y.

The equations (23), (24), (25) for the typical angle variable are most useful in the form

$$\left.\begin{aligned} a + ib &= \{(a + ib)\,(a - ib)\}^{\frac{1}{2}}\,e^{iw} = e^{iw}\,\{(a - ib)\,(a + ib)\}^{\frac{1}{2}} \\ a - ib &= \{(a - ib)\,(a + ib)\}^{\frac{1}{2}}\,e^{-iw} = e^{-iw}\,\{(a + ib)\,(a - ib)\}^{\frac{1}{2}} \end{aligned}\right\} \tag{31}$$

It is necessary to evaluate the products of $(a + ib)$ and $(a - ib)$ in each case in which these equations are used. For the case when a is M_x and b is M_y we have

$$\begin{aligned}(\mathrm{M}_x + i\mathrm{M}_y)\,(\mathrm{M}_x - i\mathrm{M}_y) &= \mathrm{M}_x^2 + \mathrm{M}_y^2 - i\,(\mathrm{M}_x\mathrm{M}_y - \mathrm{M}_y\mathrm{M}_x) \\ &= \mathrm{M}^2 - \mathrm{M}_z^2 + h\mathrm{M}_z = j^2 - \tfrac{1}{4}h^2 - p^2 + hp \\ &= j^2 - p_2^2\end{aligned}$$

so that equations (31) become

$$\left.\begin{aligned} \mathrm{M}_x + i\mathrm{M}_y &= (j^2 - p_2^2)^{\frac{1}{2}}\,e^{i\phi} = e^{i\phi}\,(j^2 - p_1^2)^{\frac{1}{2}} \\ \mathrm{M}_x - i\mathrm{M}_y &= (j^2 - p_1^2)^{\frac{1}{2}}\,e^{-i\phi} = e^{-i\phi}\,(j^2 - p_2^2)^{\frac{1}{2}} \end{aligned}\right\} \tag{32}$$

The evaluation of the product $(z + i\,[k, z])\,(z - i\,[k, z])$ is not so easy. We shall evaluate the more general product $(z + i\,[k, z])\,(\zeta - i\,[k, \zeta])$, where ξ, η, ζ are three quantities satisfying the relations analogous to (4), (5) and (6).

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* This is not rigorous, but appears to be justifiable.

(and the relations corresponding to (5) and (6) for m_y and m_z) in which x, y, z have been replaced by ξ, η, ζ, as we shall need this piece of analysis later ξ, η, ζ must satisfy the relations analogous to any of the consequences of (4), (5) and (6) that do not require for their proof the fact that x, y, z commute with one another, such as (15) and (13) [provided the auxiliary assumptions (13), (18) required for the definition of k are true for the ξ, η, ζ]

We have from (15) in which m^2 is replaced by k^2,

$$k\,[k, z] + [k\ z]\,k = [k^2, z] = 2\,(m_y x - m_x y + ihz)$$

Also

$$k\,[k, z] - [k, z]\,k = ih\,[k, [k, z]] = -\,ihz$$

from (13) Hence

$$k\,[k, z] = m_y x - m_x y + \tfrac{1}{2} ihz, \qquad (33)$$

and similarly

$$k\,[k, \zeta] = m_y \xi - m_x \eta + \tfrac{1}{2} ih\zeta$$

From (4)

$$m_z z m_z \zeta = (m_x x + m_y y)\,(m_x \xi + m_y \eta),$$

so that

$$\begin{aligned}(m_y x - m_x y)\,(m_y \xi - m_x \eta) + m_z z m_z \zeta \\ = m_y\,(x m_y + y m_x)\,\xi + m_x\,(y m_x + x m_y)\,\eta \\ + m_x\,(x m_x - y m_y)\,\xi + m_y\,(y m_y - x m_x)\,\eta \\ = m_y\,(m_y x + m_x y)\,\xi + m_x\,(m_x y + m_y x)\,\eta \\ + m_x\,(m_x x - m_y y)\,\xi + m_y\,(m_y y - m_x x)\,\eta \\ = (m_x^2 + m_y^2)\,(x\xi + y\eta) - ihm_z y\xi + ihm_z x\eta\end{aligned}$$

Using these results and also (30) we find

$$\begin{aligned}k\,(k - h)\,(z + i\,[k, z])\,(\zeta - i\,[k, \zeta]) \\ = k\,(z + i\,[k, z])\,k\,(\zeta - i\,[k, \zeta]) \\ = \{k_2 z + i\,(m_y x - m_x y)\}\,\{k_1\,\zeta - i\,(m_y \xi - m_x \eta)\} \\ = (m_y x - m_x y)\,(m_y \xi - m_x \eta) + \{k_2 z + i\,(m_y x - m_x y)\}\,k_1 \zeta \\ - ik_2 z\,(m_y \xi - m_x \eta) \\ = (m_x^2 + m_y^2)\,(x\xi + y\eta) - m_z^2 z\zeta + ihm_z\,(x\eta - y\xi) \\ + k_2\,\{k_2 z + i\,(m_y x - m_x y)\}\,\zeta - ik_2 z\,(m_y \xi - m_x \eta) \\ = (k_1 k_2 - m_z^2)\,(x\xi + y\eta) + (k_2^2 - m_z^2)\,z\zeta + ihm_z\,(x\eta - y\xi) \\ - ik_2\,\{-\,(m_y x - m_x y)\,\zeta + (m_y z - ihx)\,\xi - (m_x z + ihy)\,\eta\} \\ = (k_2^2 - m_z^2)\,(x\xi + y\eta + z\zeta) + ihm_z\,(x\eta - y\xi) \\ - ik_2\,\{m_x\,(y\zeta - z\eta) + m_y\,(z\xi - x\zeta)\} \qquad (34)\end{aligned}$$

Now take ξ, η, ζ equal to x, y, z Equation (34) reduces to the simple result

$$k\,(k - h)\,(z + i\,[k, z])\,(z - i\,[k, z]) = (k_2^2 - m_z^2)\,r^2 \qquad (35)$$

§ 5 *The Transformation Equations for the System with a Single Electron*

When the system consists of a single electron the new canonical variables are in addition to r and p_r the action variables k [defined by (17)] and $p\,[=m_z]$ and the angle variables θ and ϕ [defined by (29) and (32)] With the help of (35) the transformation equation (29) may be put in the form (31) The result is

$$\left.\begin{aligned} z + i[k, z] &= rk^{-\frac{1}{2}}(k-h)^{-\frac{1}{2}}(k_2{}^2 - p^2)^{\frac{1}{2}} e^{i\theta} \\ &= rk^{-\frac{1}{2}}(k_2{}^2 - p^2)^{\frac{1}{2}} e^{i\theta} k^{-\frac{1}{2}} = rk^{-\frac{1}{2}} e^{i\theta} (k_1{}^2 - p^2)^{\frac{1}{2}} k^{-\frac{1}{2}} \\ z - i[k, z] &= rk^{-\frac{1}{2}}(k_1{}^2 - p^2)^{\frac{1}{2}} e^{-i\theta} k^{-\frac{1}{2}} = rk^{-\frac{1}{2}} e^{-i\theta}(k_2{}^2 - p^2)^{\frac{1}{2}} k^{-\frac{1}{2}} \end{aligned}\right\} \qquad (36)$$

We have already shown that the new variables satisfy all the conditions that they ought to satisfy except that $[\theta, \phi] = 0$ This relation is not very easy to prove but fortunately it is not of any dynamical importance since if it is not true our θ and ϕ would differ from the true variables conjugate to k and p only by real quantities that are functions of k and p only and are therefore constants The amplitude of x y z expressed as Fourier series will therefore not be affected

A simpler way than the one already given of proving that the transformation from the original variables to the new variables is a contact transformation is to assume that the new variables are canonical and satisfy the quantum conditions and to deduce from that that the original variables are canonical It is convenient with this method to introduce the variables

$$\begin{aligned} \xi_1 &= (k + p - \tfrac{1}{2}h)^{\frac{1}{2}} e^{\frac{1}{2}i(\theta+\phi)} &&= e^{\frac{1}{2}i(\theta+\phi)}(k + p + \tfrac{1}{2}h)^{\frac{1}{2}} \\ \eta_1 &= -i(k + p + \tfrac{1}{2}h)^{\frac{1}{2}} e^{-\frac{1}{2}i(\theta+\phi)} &&= -ie^{-\frac{1}{2}i(\theta+\phi)}(k + p - \tfrac{1}{2}h)^{\frac{1}{2}} \\ \xi_2 &= (k - p - \tfrac{1}{2}h)^{\frac{1}{2}} e^{\frac{1}{2}i(\theta-\phi)} &&= e^{\frac{1}{2}i(\theta-\phi)}(k - p + \tfrac{1}{2}h)^{\frac{1}{2}} \\ \eta_2 &= -i(k - p + \tfrac{1}{2}h)^{\frac{1}{2}} e^{-\frac{1}{2}i(\theta-\phi)} &&= -ie^{-\frac{1}{2}i(\theta-\phi)}(k - p - \tfrac{1}{2}h)^{\frac{1}{2}} \end{aligned}$$

which are easily verified to be canonical and which give

$$\begin{aligned} \xi_1\eta_1 &= -i(k + p - \tfrac{1}{2}h) \qquad & \eta_1\xi_1 &= -i(k + p + \tfrac{1}{2}h) \\ \xi_2\eta_2 &= -i(k - p - \tfrac{1}{2}h) \qquad & \eta_2\xi_2 &= -i(k - p + \tfrac{1}{2}h) \end{aligned}$$

The transformation equations may now be put in the simple form

$$\left.\begin{aligned} x + iy &= -\tfrac{1}{2}rk^{-\frac{1}{2}}(\xi_1{}^2 - \eta_2{}^2)\,k^{-\frac{1}{2}} \\ x - iy &= \tfrac{1}{2}rk^{-\frac{1}{2}}(\xi_2{}^2 - \eta_1{}^2)\,k^{-\frac{1}{2}} \\ z &= \tfrac{1}{2}rk^{-\frac{1}{2}}(\xi_1\xi_2 + \eta_1\eta_2)\,k^{-\frac{1}{2}} \end{aligned}\right\} \qquad (37)$$

$$\begin{aligned} m_x + im_y &= i\xi_1\eta_2 \\ m_x - im_y &= i\xi_2\eta_1 \\ m_z &= \tfrac{1}{2}i(\xi_1\eta_1 - \xi_2\eta_2) \\ xp_x + yp_y + zp_z &= rp_r + ih, \end{aligned}$$

from which one can easily verify that x, y, z, p_x, p_y, p_z are canonical when it is assumed that the ξ's and η's are canonical Incidentally this method shows that our previous θ and ϕ do commute

Equations (37) are also the most convenient ones for evaluating the amplitudes of the various components of vibration, since they give at once

$$\left.\begin{aligned} x + iy &= -\tfrac{1}{2}r\left\{\frac{(k+p-\frac{1}{2}h)^{\frac{1}{2}}(k+p-\frac{3}{2}h)^{\frac{1}{2}}}{k^{\frac{1}{2}}(k-h)^{\frac{1}{2}}}e^{i(\theta+\phi)}\right. \\ &\qquad\left. + \frac{(k-p+\frac{1}{2}h)^{\frac{1}{2}}(k-p+\frac{3}{2}h)^{\frac{1}{2}}}{k^{\frac{1}{2}}(k+h)^{\frac{1}{2}}}e^{i(\phi-\theta)}\right\} \\ x - iy &= \tfrac{1}{2}r\left\{\frac{(k-p-\frac{1}{2}h)^{\frac{1}{2}}(k-p-\frac{3}{2}h)^{\frac{1}{2}}}{k^{\frac{1}{2}}(k-h)^{\frac{1}{2}}}e^{i(\theta-\phi)}\right. \\ &\qquad\left. + \frac{(k+p+\frac{1}{2}h)^{\frac{1}{2}}(k+p+\frac{1}{2}h)^{\frac{1}{2}}}{k^{\frac{1}{2}}(k+h)^{\frac{1}{2}}}e^{-i(\theta+\phi)}\right\} \\ z &= \tfrac{1}{2}r\left\{\frac{(k+p-\frac{1}{2}h)^{\frac{1}{2}}(k-p-\frac{1}{2}h)^{\frac{1}{2}}}{k^{\frac{1}{2}}(k-h)^{\frac{1}{2}}}e^{i\theta}\right. \\ &\qquad\left. - \frac{(k+p+\frac{1}{2}h)^{\frac{1}{2}}(k-p+\frac{1}{2}h)^{\frac{1}{2}}}{k^{\frac{1}{2}}(k+h)^{\frac{1}{2}}}e^{-i\theta}\right\} \end{aligned}\right\} \quad (38)$$

The simplicity of equations (37) is due to the fact that one can associate each component of vibration of the system with the product of two of the ξ, η variables that are not conjugate With systems of more than one electron there are too many components of vibration for this to be done, so that there are no equations corresponding to (37) for such systems

§ 6 *The Transformation Equations for the System with Two Electrons*

Consider now the case of a system with two electrons and use dashed letters such as x', p_x', m_x', k' to refer to the second electron. We take for our new variables, in addition to r, p_r, r', p_r', the action variables k [defined by (17)], k', p and j [defined by (20)], and their conjugate angle variables θ, θ', ϕ and ψ, which will now be defined

We define ϕ as before by equations (32) To define θ we must replace the z in (29) by some quantity that also satisfies (13) and that commutes with k', p and j The quantity $xm_x' + ym_y' + zm_z'$ ($= \mathbf{q} \,.\, \mathbf{m}'$ say, using the dot to denote a scalar product and $\mathbf{q}$ to denote the vector x, y, z) has the necessary properties, since

$$[k, [k, \mathbf{q} \,.\, \mathbf{m}']] = [k, [k, \mathbf{q}]] \,.\, \mathbf{m}' = -\mathbf{q} \,.\, \mathbf{m}'$$

from (18), and

$$[\mathbf{q} \,.\, \mathbf{m}', k'] = 0,$$

owing to the fact that k' commutes with m_x', m_y' and m_z', and further from (4)

$$\mathbf{q} \quad \mathbf{m}' = \mathbf{q} \quad (\mathbf{M} - \mathbf{m}) = \mathbf{q} \, . \, \mathbf{M},$$

so that

$$[\mathbf{q} \, . \, \mathbf{m}', p] = [\mathbf{q} \, . \, \mathbf{M}, \mathrm{M}_z] = [x\mathrm{M}_x + y\mathrm{M}_y, \mathrm{M}_z]$$

$$= - y\mathrm{M}_x - x\mathrm{M}_y + x\mathrm{M}_y + y\mathrm{M}_x = 0,$$

and from symmetry

$$[\mathbf{q} \quad \mathbf{m}', \mathrm{M}_x] = 0, \qquad [\mathbf{q} \quad \mathbf{m}', \mathrm{M}_y] = 0,$$

so that

$$[\mathbf{q} \quad \mathbf{m}', j] = 0,$$

as required Thus θ defined by

$$e^{i\theta} (\mathbf{q} \quad \mathbf{m}' - i [k, \mathbf{q} \quad \mathbf{m}']) e^{i\theta} = \mathbf{q} \, . \, \mathbf{m}' + i [k, \mathbf{q} \quad \mathbf{m}'] \tag{39}$$

is conjugate to k and commutes with k', p and j, and also may be proved, as in the case of a single electron, to commute with r and p, In a corresponding way we can define θ' by

$$e^{i\theta'} (\mathbf{q}' \quad \mathbf{m} - i [k', \mathbf{q}' \quad \mathbf{m}]) e^{i\theta'} = \mathbf{q}' \quad \mathbf{m} + i [k', \mathbf{q}' \quad \mathbf{m}] \tag{40}$$

To define ψ we must introduce the quantities

$$\left.\begin{aligned} \mu_x &= m_y m_z' - m_z m_y' = \mathrm{M}_y m_z' - m_y' \mathrm{M}_z = m_z' \mathrm{M}_y - \mathrm{M}_z m_y' \\ \mu_y &= m_z m_x' - m_x m_z' = \mathrm{M}_z m_x' - m_z' \mathrm{M}_x = m_x' \mathrm{M}_z - \mathrm{M}_x m_z' \\ \mu_z &= m_x m_y' - m_y m_x' = \mathrm{M}_x m_y' - m_x' \mathrm{M}_y = m_y' \mathrm{M}_x - \mathrm{M}_y m_x' \end{aligned}\right\} \tag{41}$$

We have

$$\left.\begin{aligned} [\mathrm{M}_z, \mu_x] &= [m_z, m_y m_z'] + [m_z', - m_z m_y] = - m_x m_z' + m_z m_x' = \mu_y \\ [\mathrm{M}_z, \mu_y] &= [m_z, - m_x m_z'] + [m_z', m_z m_x'] = - m_y m_z' + m_z m_y' = - \mu_x \end{aligned}\right\} \tag{42}$$

$$[\mathrm{M}_z, \mu_z] = m_y m_y' + m_x m_x' - m_x m_x' - m_y m_y' = 0, \tag{43}$$

and further

$$\boldsymbol{\mu} \quad \mathbf{m} = (m_z m_y - m_y m_z) m_x' + (m_x m_z - m_z m_x) m_y' + (m_y m_x - m_x m_y) m_z'$$

$$= - ih (m_x m_x' + m_y m_y' + m_z m_z'),$$

and

$$\boldsymbol{\mu} \quad \mathbf{m}' = m_x (m_y' m_z' - m_z' m_y') + m_y (m_z' m_x' - m_x' m_z') + m_z (m_x' m_y' - m_y' m_x')$$

$$= ih (m_x m_x' + m_y m_y' + m_z m_z'),$$

so that

$$\boldsymbol{\mu} \quad \mathbf{m} = 0. \tag{44}$$

The relations (42), (43) and (44) between μ_x, μ_y, μ_z and M_x, M_y, M_z correspond exactly to the relations (5), (6) and (4) between x, y, z and m_x, m_y, m_z, so that any consequences of (5), (6) and (4) that do not require for their proof the fact that x, y, z commute with one another can be applied directly to the μ's and

M's The equations (13), (18) are such consequences, and give when applied to the μ's just equations (21), and thus justify the definition (20) for the action variable j [The fact that (13), (18) involve an additional assumption, which may be regarded as completing the definition of k, here repeats itself, as (21) involves the corresponding additional assumption, which may be regarded as completing the definition of j] Equation (33) applied to the μ's gives in a similar way

$$j\,[j,\ \mu_z] = \mathrm{M}_y\mu_x - \mathrm{M}_x\mu_y + \tfrac{1}{2}ih\mu_z, \tag{45}$$

which will be required later

Now μ_z evidently commutes with r, p_r, r', p_r', k and k', and we have proved that it commutes with p, so that we can take it to be the quantity to be substituted for a in (23) for the definition of ψ We then get

$$e^{i\psi}\,(\mu_z - i\,[j,\ \mu_z])\,e^{i\psi} = \mu_z + i\,[j,\ \mu_z] \tag{46}$$

We have thus established all the relations necessary for the new variables to be canonical except that the angle variables commute with one another, but this, as before for the case of a single electron, is of no dynamical importance. All the new variables except p, ϕ and ψ are obviously invariant under the transformation (1)

To put the transformation equations (39) and (46) in the form (31) it is necessary to evaluate the $(a + ib)\,(a - ib)$ for each of them. For the case of (46) the analysis leading to equation (34) is directly applicable, and gives, when one writes j for k, M_x and M_y for m_x and m_y, p for m_z, and μ_x, μ_y, μ_z for x, y, z and ξ, η, ζ,

$$\begin{aligned} j\,(j - h)\,(\mu_z + i\,[j,\ \mu_z])\,(\mu_z - i\,[j,\ \mu_z]) \\ = (j_z^2 - p^2)\,(\mu_x^2 + \mu_y^2 + \mu_z^2) + ihp\,(\mu_x\mu_y - \mu_y\mu_x) \\ - ij_z\{\mathrm{M}_x\,(\mu_y\mu_z - \mu_z\mu_y) + \mathrm{M}_y\,(\mu_z\mu_x - \mu_x\mu_z)\}. \end{aligned} \tag{47}$$

We have

$$\begin{aligned} \mu_x^2 + \mu_y^2 + \mu_z^2 &= \Sigma_{xyz}\,(m_y^2 m_z'^2 + m_z^2 m_y'^2 - m_y m_z m_z' m_y' - m_z m_y m_y' m_z') \\ &= (m_x^2 + m_y^2 + m_z^2)\,(m_x'^2 + m_y'^2 + m_z'^2) \\ &\qquad - (m_x m_x' + m_y m_y' + m_z m_z')^2 \\ &\qquad + \Sigma_{xyz}\,(m_y m_z - m_z m_y)\,(m_y' m_z' - m_z' m_y') \\ &= m^2 m'^2 - (\mathbf{m}\ \ \mathbf{m}')^2 - h^2\,\mathbf{m}\ \ \mathbf{m}', \end{aligned}$$

and

$$\begin{aligned} [\mu_x,\ \mu_y] &= [\mu_x,\ m_z]\,m_x' + m_z\,[\mu_x,\ m_x'] - [\mu_x,\ m_x]\,m_z' - m_x\,[\mu_x,\ m_z'] \\ &= m_x m_z' m_x' + m_z\,(m_y m_y' + m_z m_z') \\ &\qquad - (-m_z m_z' - m_y m_y')\,m_z' + m_x m_z m_x' \\ &= (m_z + m_z')\,(m_x m_x' + m_y m_y' + m_z m_z') \\ &\qquad + (m_x m_z - m_z m_x)\,m_x' + m_y\,(m_y' m_z' - m_z' m_y') \\ &= \mathrm{M}_z\mathbf{m}\ .\ \mathbf{m}', \end{aligned}$$

as the last two terms cancel, with similar relations for $[\mu_y, \mu_z]$ and $[\mu_z, \mu_x]$ Hence the right-hand side of (47) becomes

$$\begin{aligned}
&(j_2^2 - p^2)\{m^2m'^2 - (\mathbf{m}\cdot\mathbf{m}')^2 - h^2\mathbf{m}\cdot\mathbf{m}'\} - h^2p^2\mathbf{m}\cdot\mathbf{m}' \\
&\qquad\qquad + hj_2(\mathrm{M}_x^2 + \mathrm{M}_y^2)\,\mathbf{m}\cdot\mathbf{m}' \\
&= (j_2^2 - p^2)\{m^2m'^2 - (\mathbf{m}\cdot\mathbf{m}')^2\} - h^2j_2^2\mathbf{m}\cdot\mathbf{m}' + hj_2(j_1j_2 - p^2)\,\mathbf{m}\cdot\mathbf{m}' \\
&= (j_2^2 - p^2)\{m^2m'^2 - (\mathbf{m}\cdot\mathbf{m}')^2 + hj_2\,\mathbf{m}\cdot\mathbf{m}'\}
\end{aligned}$$

Now

$$\begin{aligned}
\mathbf{m}\cdot\mathbf{m}' &= \tfrac{1}{2}(j_1j_2 - k_1k_2 - k_1'k_2') \qquad (48)\\
&= \tfrac{1}{2}(j_2^2 - k_1k_2 - k_1'k_2' + hj_2) \\
\mathbf{m}\cdot\mathbf{m}' - hj_2 &= \tfrac{1}{2}(j_2^2 - k_1k_2 - k_1'k_2' - hj_2) \\
m^2m'^2 - (\mathbf{m}\cdot\mathbf{m}' - hj_2)\,\mathbf{m}\cdot\mathbf{m}' &= k_1k_2k_1'k_2' - \tfrac{1}{4}\{(j_2^2 - k_1k_2 - k_1'k_2')^2 - h^2j_2^2\} \\
&= -\tfrac{1}{4}\{j_2^4 - 2j_2^2(k_1k_2 + k_1'k_2' + \tfrac{1}{2}h^2) \\
&\qquad + (k_1k_2 - k_1'k_2')^2\} \\
&= -\tfrac{1}{4}\{j_2^4 - 2j_2^2(k^2 + k'^2) + (k^2 - k'^2)^2\} \\
&= \tfrac{1}{4}(k, k', j_2),
\end{aligned}$$

where we have used the notation

$$\begin{aligned}
(a, b, c) &= -(a^4 + b^4 + c^4 - 2b^2c^2 - 2c^2a^2 - 2a^2b^2) \\
&= (a + b + c)(a + b - c)(a - b + c)(-a + b + c)
\end{aligned}$$

for three quantities a, b, c that commute Hence (47) reduces to

$$j(j - h)(\mu_z + i[j, \mu_z])(\mu_z - i[j, \mu_z]) = \tfrac{1}{4}(j_2^2 - p^2)(k, k', j_2) \qquad (49)$$

The evaluation of the product $(a + ib)(a - ib)$ for equation (39) is more complicated, and the method will only be indicated The product to be evaluated, namely, $(\mathbf{q}\cdot\mathbf{m}' + i[k, \mathbf{q}\cdot\mathbf{m}'])(\mathbf{q}\cdot\mathbf{m}' - i[k, \mathbf{q}\cdot\mathbf{m}']$, is composed of the sum of three terms like

$$m_x'^2(x + i[k, x])(x - i[k, x]),$$

and three terms like

$$\{m_x'm_y'(x + i[k, x])(y - i[k, y]) + m_y'm_x'(y + i[k, y])(x - i[k, x])\}$$

The values of the first three terms are given directly by equation (35), while the value of the sum of the quantities $(x + i[k, x])(y - i[k, y])$ and $(y + i[k, y])(x - i[k, x])$ can be obtained by applying the linear transformation (1) to the z and m_z in (35) and equating the coefficients of $l_z m_z$ on either side. Proceeding in this way we obtain finally

$$k(k - h)(\mathbf{q}\cdot\mathbf{m}' + i[k, \mathbf{q}\cdot\mathbf{m}'])(\mathbf{q}\cdot\mathbf{m}' - i[k, \mathbf{q}\cdot\mathbf{m}']) = \tfrac{1}{4}(k_2, k', j)\,r^2 \qquad (50)$$

With the help of (49) and (50) the transformation equations (46), (39), (40) may be put in the form (31), and give

$$\left.\begin{aligned} \mu_z + i\,[j,\ \mu_z] &= \tfrac{1}{2} j^{-\frac{1}{2}} (j_2{}^2 - p^2)^{\frac{1}{2}} (k,\ k',\ j_2)^{\frac{1}{2}}\, e^{i\psi} j^{-\frac{1}{2}} \\ &= \tfrac{1}{2} j^{-\frac{1}{2}} e^{i\psi} (j_1{}^2 - p^2)^{\frac{1}{2}} (k,\ k',\ j_1)^{\frac{1}{2}} j^{-\frac{1}{2}} \\ \mu_z - i\,[j,\ \mu_z] &= \tfrac{1}{2} j^{-\frac{1}{2}} (j_1{}^2 - p^2)^{\frac{1}{2}} (k,\ k',\ j_1)^{\frac{1}{2}}\, e^{-i\psi} j^{-\frac{1}{2}} \\ &= \tfrac{1}{2} j^{-\frac{1}{2}} e^{-i\psi} (j_2{}^2 - p^2)^{\frac{1}{2}} (k,\ k',\ j_2)^{\frac{1}{2}} j^{-\frac{1}{2}} \end{aligned}\right\} \tag{51}$$

and

$$\left.\begin{aligned} \mathbf{q}\ \mathbf{m}' + i\,[k,\ \mathbf{q}\ \mathbf{m}'] &= \tfrac{1}{2} r k^{-\frac{1}{2}} (k_2,\ k',\ j)^{\frac{1}{2}}\, e^{i\theta} k^{-\frac{1}{2}} = \tfrac{1}{2} r k^{-\frac{1}{2}} e^{i\theta} (k_1,\ k',\ j)^{\frac{1}{2}}\, k^{-\frac{1}{2}} \\ \mathbf{q}\ \mathbf{m}' - i\,[k,\ \mathbf{q}\ \mathbf{m}'] &= \tfrac{1}{2} r k^{-\frac{1}{2}} (k_1,\ k',\ j)^{\frac{1}{2}}\, e^{-i\theta} k^{-\frac{1}{2}} = \tfrac{1}{2} r k^{-\frac{1}{2}} e^{-i\theta} (k_2,\ k',\ j)^{\frac{1}{2}}\, k^{-\frac{1}{2}} \end{aligned}\right\} \tag{52}$$

with corresponding relations for θ'

§ 7 *Systems with more than Two Electrons*

The extension of the transformation to systems of more than two electrons may be made as on the classical theory, as explained in § 1 The $\mathbf{M}_x$, $\mathbf{M}_y$, $\mathbf{M}_z$ of the core form the m_x', m_y', m_z' of the whole system and the j of the core forms the k' of the whole system A slight change must be made in the ψ of the core in order to change it into the θ' of the whole system, since the ψ of the core has to commute with the $\mathbf{M}_z$ of the core or m_z' of the whole system, while the θ' of the whole system need not do this, as m_z' is not an action variable, but must instead commute with the p and j of the whole system This change is made by substituting for μ_z in the defining equation (46) the scalar product of the (μ_x, μ_y, μ_z) of the core and the (m_x, m_y, m_z) of the outer electron, in the same way in which the definition of θ was changed on passing from the case of one electron to the case of two electrons by substituting $\mathbf{q}\ .\ \mathbf{m}'$ for the z in (29) This change also makes θ' invariant under the transformation (1), while the ψ of the core was not On the classical theory the geometric meaning of the change is that the ψ of the core is its azimuth about the direction of the j of the core measured from the plane containing this j and the z axis, while the θ' of the whole system is the same azimuth, but measured from the plane containing the j of the core and the j of the whole system

There are alternative ways of treating the system of more than two electrons, as one may add the angular momenta together according to different plans, for instance, one could first add the angular momenta of the two outer electrons, and then add this sum to the resultant angular momentum of the remaining ones. The suitability of the different methods depends on the relative importance of the different perturbation terms in the Hamiltonian The action variables (except p) are always related to the magnitudes of angular momenta by equations of the type (17) and (20), while the method of § 4 can always be used to find the angle variables

§ 8 *Applications. The Boundary Values of the Action Variables*

The applications which are now to be made are valid only when the Hamiltonian is such that the k, k', j, p are the true action variables or approximately so

To obtain physical results from the present theory one must substitute for the action variables a set of c-numbers which may be regarded as fixing a stationary state The different c-numbers which a particular action variable may take form an arithmetical progression with constant difference h, which must usually be bounded, in one direction at least, in order that the system may have a normal state All the terms in the Fourier expansions of the Cartesian co-ordinates that correspond to transitions from a stationary state inside the boundary to one outside must vanish It may seem that these conditions are difficult to satisfy, and that in general there would be no way of choosing the arithmetical progression to satisfy them In practice it appears to be a general rule that the conditions can be satisfied in a way of which the following example is typical

Suppose that w is an angle variable and J the conjugate action variable, and that wherever e^{iw} occurs in the transformation equations it has immediately in front of it the factor $(\mathrm{J}_2 - c)$, where c is a c-number, and wherever e^{-iw} occurs it has immediately behind it the factor $(\mathrm{J}_2 - c)$, which is equivalent to the factor $(\mathrm{J}_1 - c)$ immediately in front Then we take J to have the series of values $c + \frac{1}{2}h$, $c + \frac{3}{2}h$, $c + \frac{5}{2}h$, , which terminates at $(c + \frac{1}{2}h)$ The amplitude related to $(c + \frac{1}{2}h, c - \frac{1}{2}h)$ is given by one putting $\mathrm{J} = c + \frac{1}{2}h$ in the coefficient in front of e^{iw} or in the coefficient behind e^{-iw}, and therefore vanishes on account of the factor $(\mathrm{J}_2 - c)$. The amplitudes related to $(c + \frac{1}{2}h, c - \frac{3}{2}h)$ and $(c + \frac{3}{2}h, c - \frac{1}{2}h)$ are given by one putting $\mathrm{J} = c + \frac{1}{2}h$ and $\mathrm{J} = c + \frac{3}{2}h$ in the coefficient in front of e^{2iw}, or the coefficient behind e^{-2iw} Now e^{2iw} can occur only through

$$\{(\mathrm{J}_2 - c)\, e^{iw}\}^2 = (\mathrm{J}_2 - c)\, e^{iw}\, (\mathrm{J}_2 - c)\, e^{iw} = (\mathrm{J} - c - \tfrac{1}{2}h)\, (\mathrm{J} - c - \tfrac{3}{2}h)\, e^{2iw},$$

so that its coefficient vanishes when $\mathrm{J} = c + \frac{1}{2}h$ or $c + \frac{3}{2}h$, and similarly e^{-2iw} can occur only through

$$\{e^{-iw}\, (\mathrm{J}_2 - c)\}^2 = e^{-2iw}\, (\mathrm{J} - c - \tfrac{1}{2}h)\, (\mathrm{J} - c - \tfrac{3}{2}h)$$

In the same way e^{3iw} can occur only through

$$\{(\mathrm{J}_2 - c)\, e^{iw}\}^3 = (\mathrm{J} - c - \tfrac{1}{2}h)\, (\mathrm{J} - c - \tfrac{3}{2}h)\, (\mathrm{J} - c - \tfrac{5}{2}h)\, e^{3iw},$$

and its coefficient vanishes when $\mathrm{J} = c + \frac{1}{2}h$, $c + \frac{3}{2}h$, or $c + \frac{5}{2}h$, and so on Thus all the amplitudes in the Fourier expansions that are related to a value of J greater than c and a value less than c vanish, which justifies the series we have chosen for J We could equally well have taken the series $c - \frac{1}{2}h$, $c - \frac{3}{2}h$, $c - \frac{5}{2}h$, We may call the value $\mathrm{J} = c$ the boundary value of either series

In the same way when there is more than one action variable, J and J′ say, if e^{iw} is always preceded in the transformation equations by a coefficient with the factor $f(\mathrm{J}_2, \mathrm{J}')$, and e^{-iw} is preceded by $f(\mathrm{J}_1, \mathrm{J}')$ we may take $f(\mathrm{J}, \mathrm{J}') = 0$ to be a boundary value for J This equation, though, may also be considered as fixing a boundary value for J′, and it is therefore necessary that the factor $f(\mathrm{J}, \mathrm{J}_2')$ should always occur in front of $e^{iw'}$ and $f(\mathrm{J}, \mathrm{J}_1')$ in front of e^{-iw}

Now consider (32) and (36), the transformation equations that involve the angle variables for the system with a single electron We see that $e^{i\phi}$ is preceded by the factors $(j - p_2)^{\frac{1}{2}}$, $(j + p_2)^{\frac{1}{2}}$, which are the same as $(k - p_2)^{\frac{1}{2}}$, $(k + p_2)^{\frac{1}{2}}$, and $e^{i\phi}$ by $(k - p_1)^{\frac{1}{2}}$, $(k + p_1)^{\frac{1}{2}}$, and, further, that $e^{i\phi}$ is preceded by $(k_2 - p)^{\frac{1}{2}}$, $(k_2 + p)^{\frac{1}{2}}$ and $e^{-i\phi}$ by $(k_1 - p)^{\frac{1}{2}}$, $(k_1 + p)^{\frac{1}{2}}$ All the conditions are therefore satisfied for $k - p = 0$ and $k + p = 0$ to be boundary values of the action variables Hence for a given k, p takes the $2\,|k|$ values ranging from $|k| - \frac{1}{2}h$ to $-|k| + \frac{1}{2}h$ It may be shown that k takes half integral quantum values when the central field consists of an inverse square field of force with a small inverse cube field of force superposed (with non-relativity mechanics), and thus has the values $\pm\frac{1}{2}h$, $\pm\frac{3}{2}h$, $\pm\frac{5}{2}h$, corresponding to the S, P, D terms of spectroscopy There will thus be 1, 3, 5 stationary states for S, P, D terms when the system has been made non-degenerate by a magnetic field, in agreement with observation for singlet spectra

We have already shown the selection rules for k and p It remains to be proved that transitions from $k = \frac{1}{2}h$ to $k = -\frac{1}{2}h$ cannot occur, as these would appear experimentally as S ⟶ S transitions When k is $\pm\frac{1}{2}h$, the only possible value for p is zero, so that we have to consider only transitions for which p does not change From (36) or (38) we see that the coefficient in front of $e^{i\phi}$ in the Fourier expansion of z vanishes when one puts $k = \frac{1}{2}h$, $p = 0$, so that the transition $k = \frac{1}{2}h$ to $k = -\frac{1}{2}h$ cannot occur

For a system with two or more electrons, we see from equations (32) and (51) that $j \pm p = 0$ are boundary values for j and p, and from equations (51), (52) and the equations corresponding to (52) for θ', that $k \pm k' \pm j = 0$ are boundary values for k, k' and j Hence p takes the values from $|j| - \frac{1}{2}h$ to $-|j| + \frac{1}{2}h$, while j takes the values, when k and k' are positive, from $k + k' - \frac{1}{2}h$ to $|k - k'| + \frac{1}{2}h$, in agreement with experiment This rule applies generally for the addition of any two angular momenta

The transition $k = \frac{1}{2}h$ to $k = -\frac{1}{2}h$ is still forbidden, since when $k = \pm\frac{1}{2}h$, j can take only the value k', so that j cannot change during this transition, and from (52) the coefficient in front of e^{θ} vanishes when one puts $k = \frac{1}{2}h$, $j = k'$, on account of the factors $(k_2 + k' - j)^{\frac{1}{2}}$ or $(k_2 - k' + j)^{\frac{1}{2}}$

§ 9 *The Anomalous Zeeman Effect*

The present theory does not give any explanation of those atomic phenomena that come under the heading of duplexity, namely, the peculiar relationships of the relativity and screening doublets in the X-ray spectra, the branching rule of spectroscopy, and the anomalous Zeeman effect If, however, one adopts the usual model of the atom, consisting of a normal series electron and a core in which the ratio of magnetic moment to mechanical angular momentum is double the normal Lorentz value, then the present theory gives the correct g-formula for the energy of the stationary states in a weak magnetic field without further assumption

The energy of the atom in a magnetic field in the direction of the z-axis is proportional, with this model, to

$$m_z + 2m_z' = \mathrm{M}_z + m_z'$$

instead of to M_z, as with the normal model If the field is weak we may use perturbation theory, according to which the change in energy of the stationary states is given, to the first order, by the constant term in the Fourier expansion of the energy of the perturbation in terms of the uniformising variables for the undisturbed system We must therefore obtain the constant term in the Fourier expansion of $(\mathrm{M}_z + m_z')$ in terms of the θ, θ', ϕ and ψ We have from (45) and (41)

$$\begin{aligned} j\,[j, \mu_z] &= \mathrm{M}_y(\mathrm{M}_y m_z' - m_y'\mathrm{M}_z) - \mathrm{M}_x(m_x'\mathrm{M}_z - \mathrm{M}_x m_z') + \tfrac{1}{2}ih\mu_z \\ &= (\mathrm{M}_x^2 + \mathrm{M}_y^2 + \mathrm{M}_z^2)\,m_z' - (\mathrm{M}_x m_x' + \mathrm{M}_y m_y' + \mathrm{M}_z m_z')\,\mathrm{M}_z + \tfrac{1}{2}ih\mu_z \end{aligned}$$

From equations (51) the Fourier expansions of μ_z and $[j, \mu_z]$ contain no constant terms Hence the constant term in the expansion of m_z' is

$$\frac{\mathrm{M}_x m_x' + \mathrm{M}_y m_y' + \mathrm{M}_z m_z'}{\mathrm{M}_x^2 + \mathrm{M}_y^2 + \mathrm{M}_z^2}\mathrm{M}_z = \frac{k_1'k_2' + \frac{1}{2}(j_1j_2 - k_1k_2 - k_1'k_2')}{j_1j_2}\mathrm{M}_z,$$

using (48), and the constant term in the expansion of $\mathrm{M}_z + m_z'$ is

$$\left(1 + \frac{1}{2}\frac{j_1j_2 - k_1k_2 + k_1'k_2'}{j_1j_2}\right)\mathrm{M}_z$$

The coefficient of M_z in this expression is the g-value, and agrees with Landé's formula.*

§ 10 *The Relative Intensities of the Lines of a Multiplet*

The amplitude of vibration of an atom corresponding to transitions from the state $J_r = n_r h$ to the state $J_r = (n_r - \alpha_r)h$ is obtained by one putting $J_r = n_r h$ in the coefficient in front of $\exp i\Sigma\alpha_r w_r$ in the Fourier expansion of the total polarisation of the atom, or by putting $J_r = (n_r - \alpha_r)h$ in the coefficient behind this exponential We cannot actually determine the amplitudes at present because we do not know the action and angle variables corresponding to the r's and p_r's If, however, we assume that the Fourier expansion of r does not involve p, j, ϕ or ψ, then when x/r, y/r, z/r are expanded as Fourier series in $e^{i\phi}$, $e^{i\psi}$, the ratios of the coefficients will give the ratios of the corresponding amplitudes We can thus determine the relative intensities of the lines of a multiplet and of the components into which these lines are split in a weak magnetic field †

For the case of a system with a single electron, equations (38) give at once the relative amplitudes of the components in a magnetic field For the case of the core-series electron atom we must obtain the Fourier expansions of x, y, z from (32), (51) and (52) It is convenient to introduce the quantities

$$\lambda_x = M_y z - yM_z = zM_y - M_z y = M_y z - M_z y - ihx$$
$$\lambda_y = M_z x - zM_x = xM_z - M_x z = M_z x - M_x z - ihy$$
$$\lambda_z = M_x y - xM_y = yM_x - M_y x = M_x y - M_y x - ihz$$

We have

$$M_x\lambda_x + M_y\lambda_y + M_z\lambda_z = \Sigma_{xyz}\{(M_x M_y - M_y M_x)z - ihM_z z\} = 0 \qquad (53)$$

and

$$\left.\begin{aligned} [M_z, \lambda_x] &= [M_z, M_y z - yM_z] = -M_x z + xM_z = \lambda_y \\ [M_z, \lambda_y] &= [M_z, M_x z - zM_x] = M_y z - zM_y = -\lambda_x \end{aligned}\right\} \qquad (54)$$

$$[M_z, \lambda_z] = [M_z, M_x y - xM_y] = M_y y - M_x x - yM_y + xM_x = 0 \qquad (55)$$

The relations (53), (54), (55) between the λ's and M's correspond exactly to the relations (4), (5), (6) between the x, y, z and m's or relations (44), (42), (43) between the μ's and M's We can therefore apply results deduced from (4), (5), (6) directly to the λ's We thus obtain, corresponding to (33) or (45)

$$j[j, \lambda_z] = M_y\lambda_x - M_x\lambda_y + \tfrac{1}{2}ih\lambda_z, \qquad (56)$$

---

* Landé, 'Zeits f Phys.' vol 15, p 189 (1923)

† The relative intensities of the components of a line in a magnetic field have been obtained by Born, Heisenberg and Jordan (*loc cit*) by their matrix method.

and also we can take $\lambda_x, \lambda_y, \lambda_z$ to be the $\xi\ \eta\ \zeta$ of equation (34) and can write $\mu_x, \mu_y\ \mu_z$ for $x\ y\ z$ provided we replace $m_x, m_y, m_z\ k$ by $\mathrm{M}_x, \mathrm{M}_y, \mathrm{M}_z\ j$ This gives

$$
\begin{aligned}
j\,(j-h)\,&(\mu_z + i\,[j\ \ \mu_z])\,(\lambda_z - i\,[j\ \ \lambda_z])\\
&= (j_2^2 - p^2)\,(\mu_x\lambda_x + \mu_y\lambda_y + \mu_z\lambda_z) + ih\mathrm{M}_z\,(\mu_x\lambda_y \quad \mu_y\lambda_x)\\
&\qquad\qquad - ij_2\{\mathrm{M}_x\,(\mu_y\lambda_z - \mu_z\lambda_y) + \mathrm{M}_y\,(\mu_z\lambda_x - \mu_x\lambda_z)\}
\end{aligned}
\tag{57}
$$

Now

$$
\begin{aligned}
\mu_x\lambda_x + \mu_y\lambda_y + \mu_z\lambda_z &= \Sigma_{xyz}\,(m_z\,m_y - m_y\,m_z)\,(\mathrm{M}_y z - \mathrm{M}_z y - ihx)\\
&= \Sigma_{xyz}\,\{(m_z\,m_y - m_y\,m_z)\ \mathrm{M}_y - (m_x\,m\ \ - m_z\,m_x)\,\mathrm{M}_x\\
&\qquad\qquad - ih\,(m_y\,m_z - m_z\,m_y)\}z\\
&= \Sigma_{xyz}\{m_z\ (m_x\mathrm{M}_x + m_y\mathrm{M}_y + m_z\mathrm{M}_z)\\
&\qquad\qquad - (m_x\ \mathrm{M}_x + m_y\ \mathrm{M}_y + m_z\ \mathrm{M}_z)m_z\}z\\
&= \Sigma_{xyz}\{(m_x\mathrm{M}_x + m_y\mathrm{M}_y + m_z\mathrm{M}_z)\,m_z\\
&\qquad + m_x\,(m_z\,\mathrm{M}_x - \mathrm{M}_x m_z\,) + m_y\,(m_z\,\mathrm{M}_y - \mathrm{M}_y m_z\,)\}\,z\\
&= \mathbf{m}\ \ \mathrm{\mathbf{M}}\ \ \mathbf{m}\quad \mathbf{q} + ih\,\boldsymbol{\mu}\ \ \mathbf{q}
\end{aligned}
$$

Also

$$
\begin{aligned}
\mu_z\lambda_y - \mu_y\lambda_z - \mu_x\,(x\mathrm{M}_z - \mathrm{M}_x z) &- \mu_y\,(\mathrm{M}_y z - y\mathrm{M}_z)\\
&- (\mu_x x + \mu_y y + \mu_z z)\,\mathrm{M}_z - (\mu_x\mathrm{M}_x + \mu_y\mathrm{M}_y + \mu_z\mathrm{M}_z)\,z\\
&- \boldsymbol{\mu}\ \ \mathbf{q}\mathrm{M}_z
\end{aligned}
$$

and similarly

$$
\begin{aligned}
\mu_y\lambda_z \quad \mu_z\lambda_y \quad \boldsymbol{\mu}\ \ \mathbf{q}\mathrm{M}_x\\
\mu_z\lambda_x - \mu_x\lambda_z - \boldsymbol{\mu}\ \ \mathbf{q}\mathrm{M}_y
\end{aligned}
$$

while

$$
\begin{aligned}
\boldsymbol{\mu}\ \ \mathbf{q} &= \Sigma_{xyz}\,(m_y m_z \quad m_z m_y\,) \quad \Sigma_{xyz}\,(m_y x - m_x y)\,m\\
&= k\,[k\ \ \mathbf{q}\ \ \mathbf{m}\,] \quad \tfrac{1}{2}ih\mathbf{q}\ \ \mathbf{m}
\end{aligned}
$$

from (33) Using these results and the fact that $\mathrm{M}_x\ \mathrm{M}_y\ \mathrm{M}_z$ commute with $\boldsymbol{\mu}\ \ \mathbf{q}$ (since they commute with k and with $\mathbf{q}\ \ \mathbf{m}$) equation (57) becomes

$$
\begin{aligned}
j\,(j-h)\,&(\mu_z + i\,[j\ \ \mu_z])\,(\lambda_z - i\,[j\ \ \lambda_z])\\
&= (j_2^2 - p^2)\,(\mathbf{m}\ \ \mathrm{\mathbf{M}}\ \ \mathbf{q}\ \ \mathbf{m}\ + ih\boldsymbol{\mu}\ \ \mathbf{q}) + i\,\{h\mathrm{M}_z^2 - j_2\,(\mathrm{M}_x^2 + \mathrm{M}_y^2)\}\ \boldsymbol{\mu}\ \ \mathbf{q}\\
&= (j_2^2 - p^2)\,(\mathbf{m}\ \ \mathrm{\mathbf{M}}\ \ \mathbf{q}\ \ \mathbf{m}\ + ih\boldsymbol{\mu}\ \ \mathbf{q} - ij_1\boldsymbol{\mu}\ \ \mathbf{q})\\
&= \tfrac{1}{2}\,(j_2^2 - p^2)\,\{(j_1 j_2 + k^2 - k^2)\,\mathbf{q}\ \ \mathbf{m}\\
&\qquad\qquad - 2ij_2\,(k\,[k\ \ \mathbf{q}\ \ \mathbf{m}\,] - \tfrac{1}{2}ih\mathbf{q}\ \ \mathbf{m}\,)\}\\
&= \tfrac{1}{4}\,(j_2^2 - p^2)\,\{(k + k\ + j_2)(k - k\ + j_2)\,(\mathbf{q}\ \ \mathbf{m}\ - i\,[k\ \ \mathbf{q}\ \ \mathbf{m}'])\\
&\qquad\qquad - (k + k\ - j_2)\,(-k + k' + j_2)\,(\mathbf{q}\ \ \mathbf{m}\ + i\,[k\ \ \mathbf{q}\ \ \mathbf{m}'])\}
\end{aligned}
$$

Now substitute for $\mu_z + i[j, \mu_z]$, $\mathbf{q}\ \ \mathbf{m}' - i[l, \mathbf{q}\,.\,\mathbf{m}']$ and $\mathbf{q}\ \ \mathbf{m}' + i[k, \mathbf{q}\,.\,\mathbf{m}']$ their values given by (51) and (52).

After cancelling certain factors and taking the $e^{i\psi}$ over to the right-hand side, we obtain

$$\lambda_z - i[j, \lambda_z] = r\frac{(j_1{}^2 - p^2)^{\frac{1}{2}} j_1{}^{\frac{1}{2}}}{j^{\frac{1}{2}}(j+h)^{\frac{1}{2}}}\{\mathrm{F}_{+1}\, e^{-i(\theta+\psi)} - \mathrm{F}_{+1}{}' e^{i(\theta-\psi)}\}, \tag{58}$$

where

$$\mathrm{F}_{+1} = \tfrac{1}{4}(k+k'+j+\tfrac{1}{2}h)^{\frac{1}{2}}(k-k'+j+\tfrac{1}{2}h)^{\frac{1}{2}}(k+k'+j+\tfrac{3}{2}h)^{\frac{1}{2}}(k-k'+j+\tfrac{3}{2}h)^{\frac{1}{2}} \\ + (j+\tfrac{1}{2}h)^{\frac{1}{2}} k^{\frac{1}{2}}(k+h)^{\frac{1}{2}},$$

$$\mathrm{F}_{+1}{}' = \tfrac{1}{4}(k+k'-j-\tfrac{1}{2}h)^{\frac{1}{2}}(-k+k'+j+\tfrac{1}{2}h)^{\frac{1}{2}}(k+k'-j-\tfrac{3}{2}h)^{\frac{1}{2}}(-k+k'+j+\tfrac{3}{2}h)^{\frac{1}{2}} \\ + (j+\tfrac{1}{2}h)^{\frac{1}{2}} k^{\frac{1}{2}}(k-h)^{\frac{1}{2}}$$

Similarly it may be shown that

$$\lambda_z + i[j, \lambda_z] = r\frac{(j_2{}^2 - p^2)^{\frac{1}{2}} j_2{}^{\frac{1}{2}}}{j^{\frac{1}{2}}(j+h)^{\frac{1}{2}}}\{\mathrm{F}_{-1}{}' e^{i(\theta+\psi)} - \mathrm{F}_{-1}\, e^{-i(\theta\quad\psi)}\} \tag{59}$$

where $\mathrm{F}_{-1}{}'$, F_{-1} are the quantities obtained by writing $-h$ for h in F_{+1}, $\mathrm{F}_{+1}{}'$, respectively. Also from (52)

$$\mathbf{q}\ \ \mathbf{m}' = r(j_1 j_2/j)^{\frac{1}{2}}(\mathrm{F}_0\, e^{-i\theta} + \mathrm{F}_0{}' e^{i\theta}) \tag{60}$$

where

$$\mathrm{F}_0 = \tfrac{1}{4}j^{\frac{1}{2}}(k+k'+j+\tfrac{1}{2}h)^{\frac{1}{2}}(k+k'-j+\tfrac{1}{2}h)^{\frac{1}{2}}(k-k'+j+\tfrac{1}{2}h)^{\frac{1}{2}}(-k+k'+j-\tfrac{1}{2}h)^{\frac{1}{2}} \\ - j_1{}^{\frac{1}{2}} j_2{}^{\frac{1}{2}} k^{\frac{1}{2}}(k+h)^{\frac{1}{2}}$$

and $\mathrm{F}_0{}'$ is the quantity obtained by writing $-h$ for h in F_0.

From (56)

$$\begin{aligned} j[j, \lambda_z] &= \mathrm{M}_y(\mathrm{M}_y z - y\mathrm{M}_z) - \mathrm{M}_x(x\mathrm{M}_z - \mathrm{M}_x z) + \tfrac{1}{2}ih\lambda_z \\ &= (\mathrm{M}_x{}^2 + \mathrm{M}_y{}^2 + \mathrm{M}_z{}^2)z - (\mathrm{M}_x x + \mathrm{M}_y y + \mathrm{M}_z z)\mathrm{M}_z + \tfrac{1}{2}ih\lambda_z \end{aligned}$$

Hence

$$j_1 j_2 z = \mathbf{q}\ \ \mathbf{m}' p - \tfrac{1}{2}ih\lambda_z + j[j, \lambda_z].$$

or

$$z = \frac{p}{j_1 j_2}\mathbf{q}\ \ \mathbf{m}' + \tfrac{1}{2}i\frac{1}{j_1}(\lambda_z - i[j, \lambda_z]) - \tfrac{1}{2}i\frac{1}{j_2}(\lambda_z + i[j, \lambda_z]) \tag{61}$$

Also we have

$$\begin{aligned} (x+iy)(\mathrm{M}_x - i\mathrm{M}_y) &= x\mathrm{M}_x + y\mathrm{M}_y + i(y\mathrm{M}_x - x\mathrm{M}_y) \\ &= \mathbf{q}\ \ \mathbf{m}' - pz + i(\lambda_z - ihz) \\ &= \frac{j_1 j_2 - p(p-h)}{j_1 j_2}\mathbf{q}\ \ \mathbf{m}' + \tfrac{1}{2}i\frac{j_1 - (p-h)}{j_1}(\lambda_z - i[j, \lambda_z]) \\ &\qquad + \tfrac{1}{2}i\frac{j_2 + p - h}{j_2}(\lambda_z + i[j, \lambda_z]) \end{aligned}$$

using (61). Now take the factor $(\mathrm{M}_x - i\mathrm{M}_y)$ over to the right-hand side, and substitute for $(\mathrm{M}_x - i\mathrm{M}_y)^{-1}$ its value from equations (32), namely, $(j^2 - p_2^2)^{-\frac{1}{2}} e^{i\phi}$. The result after rearrangement of the factors is

$$x + iy = \left\{\frac{(j^2 - p_2^2)^{\frac{1}{2}}}{(j^2 - \frac{1}{4}h^2)} \mathrm{q}\ \mathrm{m}' + \tfrac{1}{2}i \frac{(j - p + \frac{3}{2}h)^{\frac{1}{2}}}{j_1 (j + p + \frac{1}{2}h)^{\frac{1}{2}}} (\lambda_x - i[j, \lambda_x]) \right.$$

$$\left. + \tfrac{1}{2}i \frac{(j + p - \frac{3}{2}h)^{\frac{1}{2}}}{j_2 (j - p - \frac{1}{2}h)^{\frac{1}{2}}} (\lambda_x + i[j, \lambda_x])\right\} e^{i\phi} \qquad (62)$$

To obtain the Fourier expansions of x/r, y/r, z/r it is now only necessary to substitute for the factors $\mathrm{q}\ \mathrm{m}'$, $\lambda_x - i[j, \lambda_x]$, and $\lambda_x + i[j, \lambda_x]$ in (61) and (62), their values given by (60), (58) and (59). The ratios of the amplitudes obtained in this way are in complete agreement with those previously obtained by Kronig and others* by means of certain special assumptions, and in agreement with experiment. The F_{+1}, F_{-1}, F_0 of the present paper are proportional to the square roots of Kronig's F_{+1}, F_{-1}, $\frac{1}{2}\mathrm{F}_0$.

My thanks are due to Mr. R. H. Fowler, F.R.S., for his criticism and help in the writing of this paper.

Summary

The new quantum mechanics which involves non-commutative algebra is applied to the problem of a number of electrons moving in an approximately central field of force, a contact transformation being obtained to a set of variables which includes the k for each electron and the j of the whole system. It is found that each k is not equal to m, the magnitude of the angular momentum of the electron, as on the classical theory, but must be related to m by the formula $m^2 = (k + \frac{1}{2}h)\ (k - \frac{1}{2}h)$, and a similar relation holds between j and the resultant angular momentum of the whole system.

It is shown that the theory gives the correct boundary values for the j of the resultant of two angular momenta whose k's are given, and also gives the correct g-formula for the energy levels of an atom in a weak magnetic field on the assumption of the usual magnetic anomaly of the core of the atom. The theory also, gives Kronig's results for the relative intensities of the lines of a multiplet and their components in a weak magnetic field.

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* Kronig, 'Zeits. f. Phys.,' vol. 31, p. 885 (1925); Sommerfeld and Hönl, 'Sitz. d. Preuss. Akademie,' p. 141 (1925); Russell, 'Proc. Nat. Academy Sciences, U.S.A.,' vol. 11, p. 314 (1925).

On the Flow of Gases at High Speeds

By T E Stanton, F R S

(Received March 29, 1926)

[Plates 6 and 7]

In a paper on the discharge of gases under high pressures* the late Lord Rayleigh called attention to the deficiencies in the present state of knowledge of the characteristics of the flow of a gas, from a vessel in which it is compressed, through an orifice into the atmosphere or into a receiver at a lower pressure, and suggested that further study was desirable in the direction of investigating the accuracy of the common assumptions of the adiabatic character of the flow and its dependence on the pressure in the receiver

Assuming adiabatic flow the values of the velocity of the jet and the rate of discharge are given by the well-known relations—

$$\frac{u^2}{2} = \frac{\gamma}{\gamma - 1} \frac{p_0}{\rho_0} \left\{1 - \left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}}\right\}, \tag{1}$$

$$w = g\text{A} \sqrt{\frac{2\gamma}{\gamma - 1} \, p_0\rho_0 \left(\frac{p}{p_0}\right)^{\frac{2}{\gamma}} \left\{1 - \left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}}\right\}}, \tag{2}$$

where u is the speed, p and A the pressure and area of the jet, and w the rate of discharge, the suffix $_0$ referring to the conditions inside the discharging vessel where $u = 0$

It may be recalled that St Venant and Wantzel† were the first to obtain the equations of discharge in the forms given in (1) and (2) and to attempt a verification of them by experiment In discussing the value of the theoretical discharge they appear to have ignored the possibility of any variation in the area of the jet and to have confined their attention to the pressure and velocity changes in the plane of the least section of the orifice In this section it is apparent from (2) that as the value of p diminishes, p_0 remaining constant, the value of w rises to a maximum when p reaches the value $p_0\left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma-1}}$ and then diminishes indefinitely with further reduction of the orifice pressure, as a result of the continual reduction of the density with fall of pressure and the finite character of the velocity apparent from (1) If, therefore, the pressure in the plane of the orifice is sensibly that of the receiver, the absurd conclusion is reached that the discharge into a vacuum must be zero Such an effect was so manifestly opposed to experience that it was decided to investigate the matter experimentally For this purpose air at atmospheric pressure was allowed to enter a previously exhausted receiver by means of an orifice, and the rate of discharge was determined from observations of the pressure and temperature of the air in the receiver at equal intervals of time

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* 'Phil. Mag,' vol 32, p. 177 (1916)

† 'Journal de l'Ecole Polytechnique,' vol. 16, 1839

The results of these experiments showed that the rate of discharge increased as the ratio of the receiver pressure (here called p_r) to the initial pressure diminished from unity to 0 4, but that when the latter stage was reached further reduction in the receiver pressure had no effect on the rate of discharge which remained constant They concluded, therefore, that no identity could exist between the pressure in the receiver and the pressure of the jet in the plane of the least section or throat of the orifice for values of p_r/p_0 between zero and 0 4

These observations were subsequently confirmed by R D Napier* and H Wilde,† who observed the rate of discharge to become constant at values of p_r/p_0 in the neighbourhood of 0 5 No further advance, however, was made in the theory of orifice discharge until 1885, when Osborne Reynolds,‡ who apparently was not familiar with the work of St Venant and Wantzel, obtained similar expressions to (1) and (2) for the velocity and rate of discharge in an attempt to explain the observations of Wilde, but made, in addition, two important deductions from these relations which had escaped the notice of these workers In the first place, instead of considering a continuous fall of pressure in the throat of the orifice, Reynolds assumed a continuous fall of pressure along the axis of the jet, and treated A in equation (2) as the variable, w and p_0 being constant This at once led to the condition $p = p_0 \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma - 1}}$ at a minimum section of the jet Following the characteristics of the flow as the pressure in the receiver was gradually reduced from a value equal to that in the discharging vessel, it could, therefore, be regarded as made up of a series of streams in the discharging vessel converging towards the orifice and emerging into the receiver firstly in the form of a parallel jet, the pressure in which was sensibly equal to that of the receiver, and then when the pressure had attained the value $p = p_0 \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma - 1}}$, here called the critical pressure, developing a minimum section and expending further down stream until its pressure had reached that of the receiver Further from general considerations of the curvature of the streams, it appeared that the position of the minimum section would be down stream relative to the plane of the orifice

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* 'Discharge of Fluids,' Napier

† 'Proc. Manchester Lit and Phil. Soc.,' 1885

‡ 'Proc Manchester Lit and Phil. Soc.,' 1885; 'Phil Mag.,' March, 1886.

In the second place, by remarking that the theoretical velocity of the jet at the minimum section was that of sound under the conditions existing at that section, Reynolds perceived that when this velocity was reached no further reduction of pressure in the receiver could affect the distribution of pressure and velocity on the upstream side of the minimum section, and concluded that the rate of discharge would then remain constant The phenomenon of constant rate of discharge observed by St Venant and Wantzel was, therefore, explained on theoretical grounds

It may be remarked that this argument assumes that the area of the minimum section of the jet remains entirely unaffected by the conditions of pressure in the receiver It is, however, conceivable that, when once the velocity of sound had been attained, further reduction in the pressure of the receiver might affect the position and also the diameter of the minimum section then established Neglecting for the present this possibility, it will be recognised that the work of Reynolds placed the theory of orifice discharge on a satisfactory basis as affording an explanation of the observed facts An outstanding problem was the relation between the receiver pressure and that at the minimum section of the jet, and on this the large amount of experimental data available might be expected to throw some light, but on examination it was found that all this work consists of measurements of the receiver pressure corresponding to the commencement of a constant rate of discharge, and no measurement of the pressure of the jet appears to have been made

The results obtained by the early workers, St Venant and Wantzel, Napier and Wilde, all seem to agree in indicating that a constant rate of discharge is obtained when the receiver pressure is of the order of the theoretical value for the pressure at the minimum section, i e, p_r = 0 527 p_0, and this would appear to confirm the view of Reynolds that prior to this stage the flow consisted of a parallel jet at a pressure equal to that of the receiver and also his tacit assumption that, when the critical pressure had been reached in the jet and the minimum section established, no further reduction in the receiver pressure would affect the area On the other hand, some recent careful determinations by Hartshorn,* undertaken at the suggestion of Lord Rayleigh, have exhibited a marked divergence, from the theoretical limit, of the value of the

* 'Roy Soc. Proc.,' A, vol. 94 (1917).

receiver pressure when the rate of discharge has become constant Some of the results of Hartshorn's experiments are shown in fig 1, in which the ordinate is the pressure difference between the atmosphere and that of the reservoir supplying the nozzle, and is taken to be a measure of the rate of discharge It will be seen that in the case of a thin-lipped orifice the rate of discharge did not become constant until the receiver pressure was reduced to one-fifth of the initial pressure In discussing Hartshorn's results it must be borne in mind that they were essentially small scale experiments, the diameter of the throats of the orifices being of the order of 1 mm , and that their characteristics might be affected to some small extent by viscosity and heat conductivity which have been found by Buckingham and Edwards* to have an appreciable effect on the flow through the orifices used in Bunsen's effusion method of determining the relative densities of gases The orifices in this apparatus are, however, approximately 0 06 mm in diameter, so that such effects might reasonably be expected to be negligibly small in the orifices used by Hartshorn Apart from this consideration, the results of Hartshorn's experiments appear to afford evidence of an effect of the receiver pressure on the discharge which has not hitherto been suspected, and this view is strengthened from an examination of the accuracy of the method adopted by Hartshorn for detecting variations in the rate of the discharge which enabled him to detect variations of the order of $0 \cdot 1$ per cent It is clear from the form of the curve (3) in fig 1, with the very large exaggeration of the vertical scale, that observations of an accuracy of, say, 1 per cent, which may be regarded as in all probability that

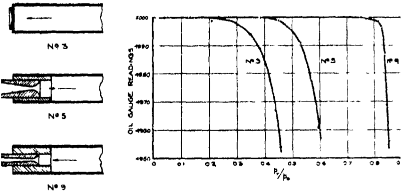

FIG 1

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* 'Scientific Papers of Bureau of Standards,' No. 359

of the earlier measurements, would suggest a critical value of the receiver pressure in the neighbourhood of 0 5

The results of Hartshorn's experiments with diverging nozzles of various angles of divergence are also exhibited in fig 1, from which it will be seen that the range of constant rate of discharge extended, for small angles of divergence, from $p_r/p_0 = 0$ to $p_r/p_0 = 0\ 8$ It is certain that when the latter stage was reached these nozzles could not have been "running full," for in that case the pressure at the outlet of the nozzle would have been considerably below the value of 0 5 instead of above it It appears probable, therefore, that at this stage the jet in the region between the throat and the outlet of the nozzle was surrounded by a stream tending to move in the opposite direction down the gradient in pressure from the receiver to the throat Whatever be the explanation of these results, the general impression derived from Hartshorn's experiments is that the receiver pressure is a factor affecting the rate of flow, and the desirability of further experimental work mentioned above is emphasized

It was decided, therefore, to undertake an experimental study of the distribution of pressure and velocity in jets flowing through orifices of different forms, with special reference to the following points on which the above discussion shows that further evidence is required —

(1) The existence of a minimum section of the jet and its variation in position and magnitude

(2) The relation between the pressure in the receiver and the pressure in the jet for increasing and constant rates of discharge.

(3) The possibility of the characteristics of high speed jets being affected by the dimensions of the orifice and the viscosity of the air

The above investigations form Part I of the present paper

Part II is devoted to a study, also suggested by Lord Rayleigh in the paper to which reference has been made, of the motion of jets at speeds above the velocity of sound, and the nature of the wave motion set up on their emergence into quiescent air

PART I.

Section I —The Characteristics of Jets from orifices of different form in the region of the critical pressure.

For this purpose observations were made of the pressure distribution in the jet along and at right angles to the axis and of the variation in its lateral dimensions, with distance from the plane or throat of the orifice

For convenience of observation these experiments were made on jets discharged into the open air from a vessel of about 200 cubic feet capacity supplied with compressed air from a 50 h p Brotherhood Compressor The general arrangement of the apparatus is shown in fig 2 The air from the vessel is admitted into a cylindrical box, fitted with guide blades to damp out the eddies

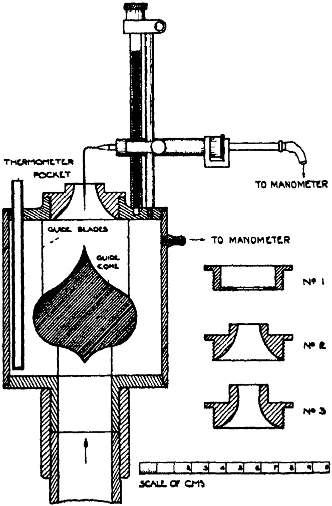

Fig 2

and irregularities of flow, so that a steady supply of air at a known pressure is delivered to the orifice which is screwed into the cover of the box A bracket is attached to the outside of the box, and carried the pressure tube which is provided with a micrometer to enable readings to be taken along and perpendicular to the axis of the jet Three forms of orifice were used—No 1, a circular hole in a thin flat plate, No 2, a plain nozzle having a faired entry and parallel outlet, and No 3, a diverging nozzle having a faired entry and a diverging outlet consisting of a cone of total angle 3° 34′ These are shown in fig 2 For a study of the effect of the linear dimensions of the orifice two thin-lipped orifices were used—one 0 61 cm. diam and the other 1 22 cms diam

(a) *Axial Distribution of Pressure* —The results of the observations of the pressure along the axis of the jet are given in Table I, and are shown plotted in fig 3, in which the thin lines indicate the pressure variation at different values of the ratio of the atmospheric pressure to that of the discharging vessel, *i e* p_r/p_0, and the thick lines the position on the axis of the jet at which the theoretical critical pressure 0 527 p_0 was reached It will be seen that this position depends on the shape of the orifice and within limits on the initial pressure of the jet In the case of the diverging nozzle the position appears to coincide, within the limits of accuracy of the observations, with that of the throat of the orifice, and is approximately independent of the initial pressure of the jet within the range of observations On the other hand, in the case of the plain nozzle and the thin-lipped orifices the position at which the critical pressure is reached is in all cases appreciably down stream relative to the throats, this divergence appearing to diminish to a definite limit as the value of p_r/p_0 is diminished On referring to the curves for the thin-lipped orifices it will be seen that this limiting position is reached for a value of p_r/p_0 of the order of 0 28, which is roughly in agreement with the value of the ratio at which the limiting value of the discharge was reached in Hartshorn's experiments with an orifice of this type. It would appear, therefore, that the stage in Hartshorn's experiment on the thin-lipped orifice between values in p_r/p_0 from 0 5 to 0 2, in which a small increase in the rate of discharge was noted, corresponds with a definite change in the position of the section of critical pressure.

The distance of the limiting position of the section of critical pressure from the throat of the orifice is approximately 0 25 R for the plain nozzle and 0 4 R for the thin-lipped orifice, where R is the radius of the throat.

The comparison of the results from the geometrically similar thin-lipped orifices (fig 3) are of interest in showing that for orifices of these dimensions

Table I.—Pressure Distribution along axis of jet discharged into atmosphere

Absolute Pressures in cms of Mercury										Description of Nozzle.
Initial.	Distance from plane of throat in cms.*									
	−0 127	−0 064	0	+0 064	+0 127	+0 190	0 254	0 317	0 380	
151 8	—	—	125 2	110 0	95 6	83 3	—	—	—	0 61 cm. thin lipped orifice, similar to No. 1, fig 2.
176 2	—	—	144 3	126 2	106 4	87 6	—	—	—	
201 5	—	—	163 2	141 2	116 5	92 9	—	—	—	
224 0	—	—	178 2	148 8	121 4	92 3	—	—	—	
250 5	—	—	200	170 8	138 2	106 4	—	—	—	
150 8	—	—	—	—	—	94 0	86 4	81 3	76 2	1 22 thin-lipped orifice, No 1, fig 2.
175 5	—	—	—	—	111 5	102 1	91 4	83 5	75 7	
200 2	—	—	—	—	—	111 2	98·0	88 1	77 9	
250·2	—	—	—	—	147 5	131 4	113 5	100 2	86 6	
274 8	—	—	—	—	162 7	145 5	125 2	110 0	96 5	
149 2	—	94 2	89 8	85 0	80 5	—	—	—	—	1 25 cm plain converging nozzle, No 2, fig 2
198 8	—	124 9	118 8	111 9	104 6	—	—	—	—	
246 0	—	154 3	146 5	137 2	129 1	—	—	—	—	
151 0	89 8	84 6	79 2	72 5	67 4	—	—	—	—	1 21 cm. diverging nozzle, No. 3, fig 2.
175 6	104 2	97 8	91 7	83 6	77 7	—	—	—	—	
200 2	119 0	111 3	104 4	96 4	88 0	—	—	—	—	
225 6	133 7	125 0	117 2	106·5	98 4	—	—	—	—	
250 2	147 8	138·0	130 0	117 6	108 8	—	—	—	—	
275 5	164 2	151 6	142 1	129 0	119 8	—	—	—	—	

* Distances reckoned + ve down-stream

and within the limits of accuracy of the observations the similarity extends also to the pressure distribution, i e, the effect of viscosity on dynamical similarity in the motion is small *

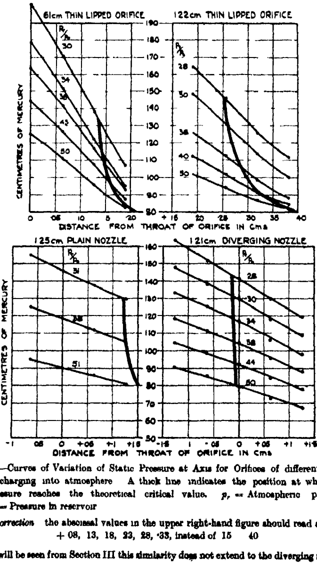

Fig 3.—Curves of Variation of Static Pressure at Axis for Orifices of different form, discharging into atmosphere A thick line indicates the position at which the pressure reaches the theoretical critical value. p_r = Atmospheric pressure p_0 = Pressure in reservoir

Correction the abscissal values in the upper right-hand figure should read as + 08, 13, 18, 23, 28, ·33, instead of 15   40

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* It will be seen from Section III this similarity does not extend to the diverging nozzles

(*b*) ***Radial Distribution of Pressure***.—The observed distribution of static pressure across that section of the jet having the critical value of the pressure at the axis is shown, for the 1·22 cms. thin-lipped orifice and the divergent nozzle in fig. 3, from which it will be seen that the falling off in the value of the static pressure near the boundary is appreciable. It might be supposed at first sight that this was a frictional effect, but as has been pointed out by previous writers,* the relatively large curvature of the individual streams near the boundary must involve a radial pressure gradient of the kind observed to which must correspond an upstream displacement of the throats of the elementary streams near the boundary.

A method of verifying this assumption which suggested itself was the measurement of the pressure in a pitot tube inserted at various points of the jet. Assuming no losses in the elementary stream in which it is placed, and provided that the velocity does not exceed that of sound, the pressure in the pitot tube should be equal to the pressure in the reservoir from which the stream emerges. If, therefore, the pressure in the stream near the wall is affected by friction, an appreciable difference between the pitot tube pressure and the reservoir would be observed. This method of discrimination was accordingly adopted, and the results of pitot tube observations on the two orifices considered are shown plotted in fig. 4. It was not possible to get an observation nearer to the walls than 0·025 cms., but for all radii less than this no variation of the pitot tube pressure was noted, and the observed value was within 0·5 per cent. of that of the

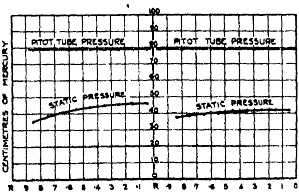

FIG. 4.—Radial Distribution of Static and Pitot Tube Pressures over minimum section of Jet.

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* Cotterill, 'Applied Mechanics,' p. 570.

receiver pressure It was concluded, therefore, that the observed falling off of the static pressure near the walls was not due to friction but to the up-stream displacement of the throat of the outside streams

(c) *The Variation in the Linear Dimensions of the Jet with Distance from the Throat of the Orifice* —The object of these experiments was three-fold, and may perhaps best be expressed in the form of the following three questions —

(1) Could the existence of a minimum section of the jet be detected for values of p_r/p_0 less than 0 527 ?

(2) If so, did its position coincide with that section at which the theoretical critical pressure was observed ?

(3) Did the area of the minimum section of the jet from a given orifice depend on the value of the ratio of the receiver pressure to the initial pressure ?

The determination of the effective boundary of the jet was obviously difficult, and after some consideration it was thought that a sufficiently accurate location of it would be the point at which the pressure in a pitot tube was a mean between that in the interior of the jet and the atmospheric pressure The method adopted, therefore, was to move the pitot tube across a diameter of the jet by means of a micrometer and measure the distance from boundary to boundary as defined above. The measurements were all made on the 1 22 cms diameter thin-lipped orifice, and the reduced values of the diameter of the jet at varying values of the initial pressure and of the distance from the plane of the orifice are given in Table II following

It will be seen that there is a well defined minimum section for all but the highest value of p_r/p_0, the value of which is so close to the critical value at which the formation of a minimum section begins that the detection of a minimum in this case could hardly be expected. Further, the areas of the minimum sections increase as the value of p_r/p_0 diminishes, and this affords an explanation of the low limit of this ratio at which the discharge became constant in Hartshorn's experiments on this type of orifice (fig 1)

On comparing the positions at which the minimum sections are located by the above method with the corresponding positions of the section at which the critical pressure exists for this nozzle, which is shown in fig 3, it will be seen that the agreement is reasonably good. It was concluded, therefore, that the answers to the above questions were all in the affirmative

Table II —**Measured** diameter of jet from 1 22 cm thin lipped orifice at varying values of the initial pressure and distance from the plane of the orifice

Distance down-stream of section from plane of orifice	0 063	0 127	0 254	0 381	0 508	0 762	1 016 cms.	Distance down-stream of minimum section from plane of orifice.	Diameter of minimum section.
								Cms	Cms
								—	—
Diam of jet at p_r/p_o = 0 488	—	1 108	1 087	1 080	1 080		1 065		
„ = 0 431	—	1 110	1 098	1 100	1 105			0 38	1 097
„ „ = 0 368	1 135	1 120	1 118	1 130	1 140			0 13	1 116
„ = 0 304	1 140	1 132	1 150	—	—			0 22	1 132

To sum up, the conclusions derived from the experiments described in the present section are as follows —

(1) In each of the three characteristic types of orifice which may be used for the discharge of gases from a vessel at constant pressure into a receiver at a pressure appreciably below the critical value 0 527 p_0, the section of the jet diminishes to a minimum value, at which the velocity is that of sound under the conditions existing, and then increases This minimum section in the case of a free jet *is not constant in area or position relative* to the plane or throat of the orifice, but depends on the total ratio of expansion

(2) In a jet in which the expansion takes place within solid boundaries, *i e*, a diverging nozzle, the minimum section may for all practical purposes be regarded as coincident with the throat of the nozzle for all ratios of expansion

(3) The flow of the fluid up to the minimum section is adiabatic in character

Section II —The Characteristics of the Rate of Discharge from Orifices of Different Forms

The results of the experiments described above on the variation in position and magnitude of the minimum section of the jet from a thin-lipped orifice afford, as was pointed out, a partial and probably a complete explanation of the low value of the ratio p_r/p_0 at which the discharge became constant for this form of orifice, in Hartshorn's experiments On the other hand, the cause of the extremely high value of the corresponding ratio in the case of the diverging nozzles was still an obscure problem, and in attempting its solution it was thought advisable in the first instance to determine whether this characteristic applied to diverging nozzles of considerably greater dimensions than those of Hartshorn, which it will be remembered were 1 mm diameter In the tests previously described on the two geometrically similar thin-lipped orifices, 0 61 and 1 22 cms diameter, no appreciable scale effect could be detected, but this might possibly be due to the absence of a solid boundary to the jet, and it was thought that for a completely enclosed jet the influence of the viscosity of the air might be much more marked It was decided, therefore, to investigate the characteristics of the discharge from the orifices used in the present work For this purpose the original method of St Venant and Wantzel, in which the flow is from the atmosphere to a variable lower pressure, possesses, as pointed out by Lord

Rayleigh,* considerable advantages over that of discharging into the atmosphere from a vessel in which the pressure was varied, and it was accordingly adopted The re-arrangement of the apparatus for the purpose was rendered comparatively easy by the device of utilising the discharging drum of the previous experiments as the receiver, by previously exhausting the latter to a low pressure and then allowing air at atmospheric pressure to pass through the nozzle into the receiver, the pressure in which would gradually rise The arrangement of the apparatus is shown in fig 5 The discharging nozzle is enclosed in an air-tight cylinder

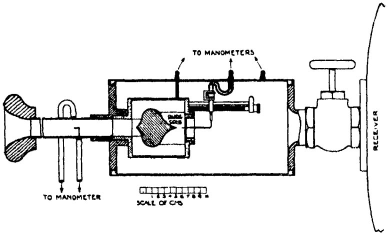

Fig 5

communicating with the receiver by means of a stop-valve The orifice box is attached to the other cover of this cylinder, and is supplied from the external air by means of a brass pipe 2 85 cms diameter and 300 cms long provided with a bell mouthpiece at the inlet and pitot and static pressure tubes near the delivery end, from observations on which the mass flow can be measured

The receiver was disconnected from the air compressor and coupled to an exhausting pump so that the pressure in it could be reduced to any desired value below atmospheric pressure A static pressure tube was inserted in the axis of the jet as shown and connected to a manometer Provision was also made for recording the pressure in the outer cylinder, i e., the receiver pressure, and the pressure in the orifice box, or the initial pressure, which was slightly below that of the atmosphere

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* l c *ante*, p. 1

In making an experiment the pressure on the drum having been reduced to a given value the exhaust pump was stopped and the valve connecting the receiver to the orifice box was opened Readings of the discharge gauge and the manometers connected to the box receiver and static pressure tube were then taken at equal intervals of time

The results proved to be of considerable interest, and gave a satisfactory explanation of the peculiar behaviour of diverging nozzles which had previously been obscure

Taking first the case of flow through a thin lipped orifice the results of the tests on the 0 615 cms diameter orifice are shown in fig 6 In this the values of the measured mass flow and the pressures at different positions along the axis of the jet have been plotted as ordinates on a base of values of the ratio of the receiver pressure to the initial pressure As regards the variation of mass flow, it will be seen that the flow becomes constant at a value of p_r/p_0 equal to 0 2, which, as will be seen from fig 1 agrees closely with the value found by Hartshorn for this case

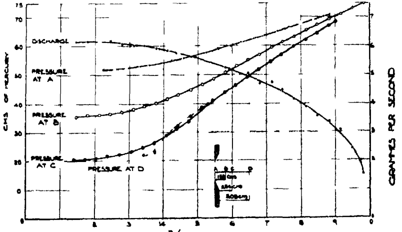

Fig 6

It would appear therefore that as predicted from the experiments on geometrically similar orifices described in Section I, the effect of linear dimensions on the limiting conditions of flow are, for this type of orifice, extremely small

The pressure curves taken at the three positions A, B C and D indicated in fig. 6, also afford a satisfactory check on the observations, described in Section I, of the movement, with variations of p_r/p_0, of the section at which the critical pressure exists It will be seen that at 40 cms of mercury, which is the critical pressure in this case, the position of the section is 0 254 cms in front of the orifice for $p_r/p_0 = 0\ 527$, and moves to a position 0 15 cms in front of it when the ratio has fallen to 0 38

It may be remarked that the change in the rate of discharge between values of p_r/p_0 of 0 2 and 0 537 taken from the curve of fig 6 is of the order of 10 per cent From Table II it will be seen that this is in close agreement with the measured changes of area of the minimum section of the jet This is satisfactory evidence that the velocity at the minimum section of the jet remains invariable, as it should do according to the theory

The results of a similar series of observations on a diverging nozzle of throat diameter 0 615 cms. and a diverging outlet of total angle 2° 52′, are shown in fig 7, in which are plotted the values of the rate of discharge, the pressure at the axis of the jet at the least section of the nozzle, and the pressures at the wall of the nozzle at two points distant respectively 1 27 and 3 81 from the throat From the curve of discharge it will be seen that this bears a close resemblance to that observed by Hartshorn for his nozzles of 4 4° and 4 6° angles of divergence in which the discharge appears to be constant up to a value of the receiver pressure equal to 80 per cent. of the initial pressure There is, however,

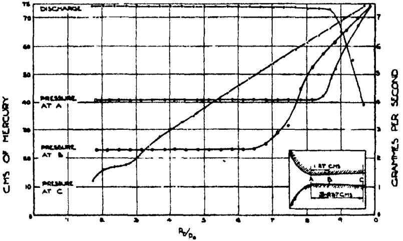

Fig 7

in the present experiments a small but perceptible fall in the discharge before this stage is reached, and corresponding with it there is also a slight increase in the throat pressure There would appear to be some evidence, therefore, that even in such completely enclosed jets as those in diverging nozzles, there is a very slight movement of the section of critical pressure down-stream as the value of p_r/p_0 increases with a consequent perceptible decrease in the discharge The plotted pressure variations at different distances along the diverging outlet throw considerable light on the action of the jet in passing through the divergence It will be seen from the figure that the pressure at a distance of 1 27 cms from the throat remains constant up to a value of p_r/p_0 of 0 65, and then begins to rise with the receiver pressure At 3 81 cms from the throat there is no steady value and the pressure rises with the receiver pressure throughout the whole range It is clear, therefore, that at no stage of the expansion does the nozzle "run full" at this distance from the orifice, and the pressure here is sensibly that of the receiver At 1 27 cms from the orifice the nozzle "runs full" up to a value of $p_r/p_0 = 0$ 65, and then breaks away from the walls As a variation on this experiment an extension piece was fitted to the end of this nozzle so that the length of the diverging cone was doubled and the observations repeated It was found that the critical pressure at the throat was not reached until the ration p_r/p_0 had attained the value of 0 90 Further, the values of p_r/p_0 at which the jet broke away from the two points to which the manometers were connected were considerably greater than those previously observed Again, on shortening the nozzle to one quarter of its original length the critical pressure at the throat was reached for a value of p_r/p_0 of 0 70 It was clear, therefore, that the critical points in the discharge and pressure curves of the nozzle were dependent upon its length As a second variation the angle of divergence of the nozzle was increased to 4° 36′, and the test repeated In this case it was found that the discharge remained constant up to a value of p_r/p_0 appreciably greater than when the angle was only 2° 52′ On increasing the angle still more the value corresponding to the critical value of the discharge receded, showing that there was a maximum value for some definite value of the diverging angle

It would appear, therefore, that in a diverging nozzle supplied with air at constant pressure the expansion ceases, i e, the nozzle fails to run full at some point in its length depending on the value of the receiver pressure, the angle of divergence, and the distance of the point from the end of the nozzle, and that as the receiver pressure rises the point of break away moves gradually up to the throat, and finally at a value of p_r/p_0 depending on the shape and dimensions of the nozzle disturbs the pressure distribution there with consequent reduction in the flow. On the down-stream side of the point of break away the region between the walls of the nozzle and the issuing jet is therefore one of back flow towards the throat of the nozzle with a pressure gradient consisting of the difference between the receiver pressure and that of the jet at the point of break away. This action affords a satisfactory explanation of all the characteristics of diverging nozzles observed by Hartshorn.

Section III.—The Existence of a Scale Effect in the Flow through Geometrically Similar Nozzles.

The effect of the changes in dimensions of the nozzle on the pressure and discharge characteristics described above raises the question whether the flow through nozzles at speeds above the velocity of sound may not be affected by the viscosity of the air since this would be a necessary accompaniment of an effect due to the linear scale of the nozzle. The results of changes in dimensions hitherto discussed, cannot, of course, be taken to prove that the conditions for dynamical similarity in the flow must include some unknown scale factor, for the reason that geometrical similarity in the various nozzles tested did not exist. In this connection it may be pointed out that the conditions for dynamical similarity of flow throughout the nozzles are :—

(1) The nozzles must be geometrically similar.

(2) At similarly situated points in the outlets (*a*) the product of the linear dimension and the speed divided by the kinematic viscosity, and (*b*) the ratio of the speed to the velocity of sound, must have identical values, *i.e.* :—

(*a*)
$$\frac{v_1 l_1}{\nu_1} = \frac{v_2 l_2}{\nu_2},$$

(*b*)
$$\frac{v_1}{V_1} = \frac{v_2}{V_2}.$$

It is generally assumed that when the speed is in the neighbourhood of the velocity of sound, as in the cases under consideration, the effect of the viscosity of the air is negligible, *i.e.*, condition (*a*) may be ignored as an essential for similarity of flow, but as far as the writer is aware, experimental evidence bearing on this point appears to be lacking. It was decided, therefore, that as the method of observation described in the last section was exceptionally suitable for testing the above assumption, a series of tests on geometrically similar diverging nozzles should be made. In such tests it was clear that, provided the initial pressure and temperature of the air supply remained constant, the pressure distributions in such nozzles should be identical for identical values of p_r/p_0, if dynamical similarity in the flow was independent of condition (*a*)

Three diverging nozzles were prepared for the tests. The diameters at the throats were 0 61, 0 305 and 0·152 cm., respectively, and pressure holes were made in the walls at distances of 2 08 and 6 46 throat diameters from the throat

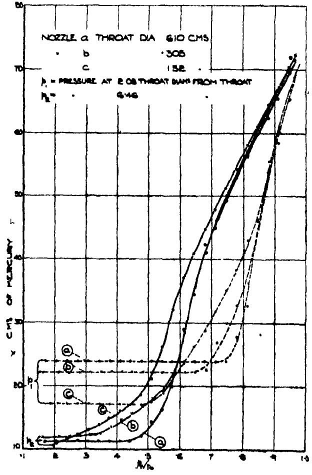

FIG. 8.—Pressures in geometrically similar diverging Nozzles.

The results of the tests on these nozzles are shown in fig 8 in which for the sake of clearness only the pressure variations at the two points in the walls corresponding to the changes in the receiver pressure are plotted

It will be seen that in the case of the pressure at the wall of the nozzle at 2 08 diameters from the throat the steady pressures in the stage during which the nozzles are running full are different in amount and the values of p_r/p_0 at which the break away of the flow from the wall takes place are also different The latter phenomenon is much more marked in the case of the pressures at 6 46 diameters from the throat At this point the largest nozzle is running full up to a value of p_r/p_0 of 0 45 whereas the flow has failed in the case of the smallest nozzle in the neighbourhood of $p_r/p_0 \simeq 0\ 10$

It is clear therefore that in these experiments dynamical similarity in the flow was not preserved and the conclusion derived from the results is that condition (*a*) above is necessary and probably sufficient for this purpose It is of interest to note that in this case instability in the flow is associated with a reduction in the value of the criterion vl/ν instead of an increase in this quantity as in the case of the breakdown of steady motion into turbulence in the case of a fluid flowing through a channel with parallel boundaries

It follows therefore that since a reduction in the value of vl/ν can equally be made by an increase in the kinematic viscosity of the fluid a similar effect to that shown in fig 8 for nozzles of different sizes should be obtained for a single nozzle in which the initial temperature of the air was varied

The possibility that the effects shown in fig 8 were due to small deviations from exact similarity in the dimensions of the nozzles was considered very remote owing to the care taken in their preparation but it was thought that a check on the results by means of a variation of the initial temperature of the air entering one of the nozzles would be of value Arrangements were therefore made for varying the initial temperature of the air by means of a coil of manganin wire through which an electric current could be circulated wound round the inlet pipe shown in fig 5 The temperature of the air was measured by mercury thermometers—one placed near the entrance to the nozzle and one at its outlet The results of two tests on the 0 152 cm diverging nozzle C — one at atmospheric temperature and the other at an initial temperature of 141° C —are shown in fig 9

It will be seen that, as predicted, the effect of a rise of temperature of the air is to move the point of "break away nearer to the throat in the same manner as a reduction in the size of the nozzle, and the results therefore confirm the conclusions derived from the previous tests

It may be remarked that the dimensions of the nozzles used for these experiments are relatively small, and it is possible that in comparatively large sizes the effect of the vl/ν factor may also be relatively small

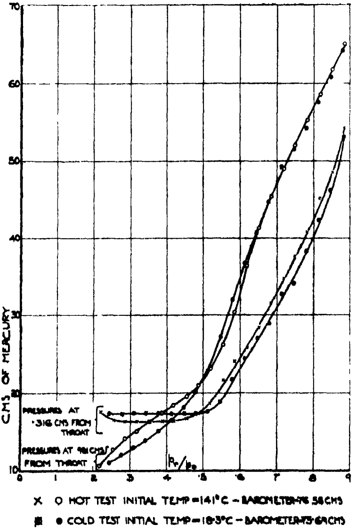

Fig 9 —Tests on 0·152 cm diverging Nozzle.

PART II—THE CHARACTERISTICS OF AIR JETS AT SPEEDS ABOVE THE VELOCITY OF SOUND

Section I – The Measurement of the Speed

In the case of gases flowing at moderate speeds, the most convenient and accurate method of measuring the velocity at a point is by means of the well-known instrument consisting of a combination of a pitot tube and static pressure tube In the use of this instrument the changes in pressure velocity and density of the air stream are supposed to be given by equation (1), which for the present purpose may be written in the form

$$\frac{u^2}{2} - \frac{u_0^2}{2} = \frac{\gamma}{\gamma - 1}\frac{p_0}{\rho_0}\left\{1 - \left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}}\right\}, \tag{3}$$

where the suffix $_0$ refers to the undisturbed conditions of the air stream Assuming that the stream is brought to rest at the mouth of the pitot tube, the pressure in the pitot tube will be given by

$$\left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}} = 1 + \frac{\gamma - 1}{2}\frac{u_0^2}{a_0^2}, \tag{4}$$

where a_0 is the velocity of sound under the conditions $p_0\rho_0$ For speeds up to 150 feet per second, where $p - p_0$ is small, the formula reduces to

$$p - p_0 = \tfrac{1}{2}\rho_0 w_0^2, \tag{5}$$

so that all that is then required for the determination of the speed is a knowledge of the density of the fluid and the pressure difference between the pitot and static pressure tubes This relation has been found to hold a high degree of accuracy over the range to which it is applicable

It might be assumed, therefore, that equation (4) might be applied to the determination of the velocity of jets moving at speeds exceeding the velocity of sound in a similar manner to that adopted for low velocity calculations It is found, however, that calculations of speed so determined are not reliable in that they give values of the speed appreciably less than the real values determined by independent methods The cause of this discrepancy was explained by the late Lord Rayleigh, who showed* that the dynamic pressure on a small obstacle placed in a stream of air moving at those speeds will not be that due solely to the adiabatic compression of the stream impinging on it, but that this compression will be divided into two stages in one of which adiabatic conditions obtain, and in the other the conditions for a stationary wave of finite disturbance From an application of Rankine's theory of thermodynamic waves of finite disturbance to the motion, Lord Rayleigh showed that the dynamic pressure measured at the centre of the obstacle would be related to the speed, density and static pressure of the air by the following relation*

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* 'Roy. Soc Proc.,' A, vol. 84 (1910).

$$\left(\frac{p_2}{p_0}\right)^{\frac{\gamma-1}{\gamma}} = \frac{(\gamma+1)^2}{4\gamma}\left(\frac{p_1}{p_0}\right)^{\frac{\gamma-1}{\gamma}}\left\{1+\frac{\gamma-1}{\gamma+1}\frac{p_0}{p_1}\right\}, \tag{6}$$

where

$$\frac{p_1}{p_0} = \frac{2\gamma}{\gamma+1}\frac{u^2}{a^2} - \frac{\gamma-1}{\gamma+1}$$

and p_2 is the observed dynamic pressure which may be the pressure in the mouth of a pitot tube facing the stream

The advantages of the use of a pitot tube for the measurement of the values of u/a at very high wind speeds were so obvious that it was decided to attempt to make an experimental verification of the accuracy of Lord Rayleigh's relation when used for this purpose

To obtain a high velocity of flow a diverging nozzle 1 27 cms diameter at the throat and having an angle of divergence of 4° 56′ was used At the end of the divergence the air passed into a short length of parallel channel and thence by an expanding cone into a pipe 7 6 cms diameter in which the mass discharge could be measured A small pitot tube was inserted at the axis near the end of the diverging cone to enable the values of p_2 to be observed This tube could be replaced by a static pressure tube for the measurement of p_0

From the observed values of p_2, p_0, and assuming a value of γ, the theoretical value of u/a could be calculated from equation (6) for any point in the cross section of the jet

As no determination of the actual value of u/a at a point to the degree of accuracy required for the calculation seemed possible, it was necessary to adopt a method of mean values such as a comparison of the mean value of u/a from the pitot tube measurements with its mean value calculated from the observed mass discharge and the density, the latter quantity being estimated from the pressure and temperature of the stream For this purpose it was essential that the nozzle should be "running full" over the experimental section, and considerable time was spent in determining a suitable angle of divergence for the nozzle and the value of the initial pressure of the air for this condition to be satisfied Finally it was found that in a nozzle of the dimensions given above, with an initial pressure not less than 220 cms of mercury, there was a continuous fall of pressure from the throat to the experimental section, and the pitot tube pressure over the whole section was sensibly constant except in the region close to the wall. It was considered, therefore, that the nozzle was running full and free from waves at the experimental section. An attempt was then made to measure the temperature of the flow by inserting thermojunctions in it, but any correct estimation of the true temperature was soon found to be hopeless owing to the heating up of the thermojunction by the adiabatic compression of the gas in its neighbourhood, a difficulty which was encountered in the well-known porous plug experiment of Joule and Thomson. This idea was accordingly abandoned, and consideration was given to the use of the well known reaction method for the determination of the momentum of the jet which, in combination with the value of the mass discharge, would give a value of the mean velocity of the jet.* This method appeared to be more promising, and the arrangement set up for the measurement of the momentum is shown in fig. 10.

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* 'Roy. Soc. Proc.,' A, vol. 84 (1910)

It will be seen that the nozzle is supplied with air by means of two india-rubber tubes connected to a tee-piece screwed into its inlet end, and rests on a narrow air-tight seating made at the entrance to the parallel discharge channel which is the same diameter as the outlet of the nozzle. A weigh beam is carried on knife edges attached to the bracket supporting the discharge channel, one of its arms carrying a scale pan and the other engaging with a pivot on the axis of the nozzle. By this means the vertical reaction of the jet could be measured.

In the first attempt at calibration the mean values of the speed and density were calculated from observations of the mean value of ρu^2 given by the weigh beam, the mean value of ρu given by the discharge meter, and the known area of the channel supposed to be running full. A mean value of a was then calculated from the observed static pressure and the calculated mean density. The rate of the mean speed to the mean value of a was then compared with the mean value of w/a obtained from the pitot and static pressure measurements. This method was, of course, open to objection that the error due to the assumption that the ratio of the mean values of w and a was equal to the mean value of the ratio might not be negligible. On further consideration it was seen that this objection could be overcome by proceeding as follows:—Assume the cross section of the jet to be divided into concentric rings of width δr and the value of u/a determined for each ring from pitot and static pressure observations.

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* Morley, 'Proc. Inst. Mech. Engineers,' 1916.

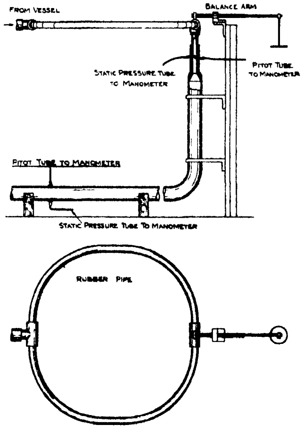

Fig 10.

in each. If the momentum of the fluid passing through each of the rings is δM we have—

$$\Sigma\, \delta M = \Sigma\, 2\pi r\, \delta r \rho u^2, \tag{7}$$

or $\Sigma\, p\gamma \frac{u^2}{a^2} 2\pi r\, \delta r = M$ the total momentum of the jet. From the observed values of p and the calculated values of u/a the summation on the left can be evaluated graphically and the extent of its agreement with the observed value of M will furnish a measure of the accuracy of the Rayleigh formula.

The observations made for the purpose of the calibration are given in Table III,

Table III —Experimental check on accuracy of Rayleigh formula for measurement of speeds above the velocity of sound

Area of Jet = 3 29 sq cms Barometer = 77 7 cms Hg

Radius of jet cms.	0 051	0 152	0 254	0 356	0 457	0 558	0 660	0 762	0 864	0 914	0 991
Static pressure, cms of Hg	19 17	19 17	19 17	19 67	19 95	19 17	18 67	18 40	1 90	17 90	18 15
Pitot tube pressure	146 7	148 0	148 7	150 0	149 5	147 5	143 3	139 0	129 8	114 7	79 4
u/a (calculated from above)	2 36	2 37	2 37	2 35	2 33	2 37	2 37	2 34	2 29	2 14	1 74

Measured reaction of nozzle by weigh beam 3,021 grammes.
Mean static pressure over section of jet (by integration) 250 grammes per sq cm.
Resultant atmospheric pressure on nozzle = 2,632 grammes.
Nett reaction of nozzle = 5 653 grammes
Value of $\Sigma\gamma p\ (u/a)^2\ 2\pi r\delta r$ by graphical integration = 5 760 grammes

Table IV —Comparison of the Values of the Velocity obtained by different methods.

Experiment No	Pressure in cms. of mercury absolute				Initial Temp °C	Measured reaction in grammes	Discharge, Grammes per second	Calculated Values.				
	Initial	At outlet		Pitot Tube at Axis.				u/a	a	v	v_s	t_m
		Axis	Wall						Cms per second			
1	260 5	20 95	19 70	153 2	23 8	5408	100	2 30	24040	54950	55370	52790
2	225 5	18 15	17 15	134 2	27 5	4840	88 0	2 39	24410	55000	56080	54180
3	201 0	24 00	29 30	119 9	18 7	3822	79 4	1 87	25180	51400	47120	47220
4	176 0	46 10	48 90	119 7	22 8	2342	69 4	1 29	28480	43300	36760	33120

in which are also given the values of the observed and calculated reactions It will be clear that in calculating the total reaction due to the jet account must be taken of the difference of static pressure between the outside and the inside of the nozzle The measured reaction is the difference between the vertical forces in the nozzle (1) before the jet is turned on and the external and internal air pressures are equal, and (2) after the jet is started when the external pressure will be atmospheric and the internal pressure the static pressure of the jet at the section considered This measured reaction must, therefore, be augmented by the product of the area of the jet and the difference between the atmospheric pressure and the static pressure of the jet As the static pressure of the jet varies across the section this quantity was evaluated by the planimeter in the usual manner It will be seen that the measured reaction is only 1 5 per cent below the calculated value which is within the accuracy of the observations It would appear, therefore, that the method here described of estimating from Lord Rayleigh's formula the value of u/a at a point in a current of air moving at a speed considerably in excess of the velocity of sound is reliable

For the estimation of the actual velocity a further determination of the temperature or density of the air at the point considered is, of course, necessary For the reasons given above this measurement is a matter of considerable difficulty, and until it is overcome it would seem that recourse must be had to the calculation of the density on the assumption of adiabatic expansion from the initial pressure and temperature in the reservoir, supposed known, to the measured pressure at the point considered, or, alternatively, the direct calculation of the speed from equation (1) The accuracy of such estimations will, of course, depend on the extent to which the flow in the jet is adiabatic in character and also on the efficiency of the nozzle, *i e*, the absence of disturbances such as stationary waves and failure of the nozzle to run full

To illustrate the kind of accuracy obtained by these methods, four experiments were made with the nozzle described above—two at values of the initial pressure at which the nozzle was known to be running full, one at an initial pressure at which the flow had commenced to break down, and one at a still lower initial pressure when the point of break away had penetrated to some distance from the outlet of the nozzle towards the throat

The observations made were —

(1) The initial pressure and temperature in the reservoir.

(2) The static pressure and pitot tube pressure at a point in the axis of the

nozzle at the outlet and also the pressure at the wall of the nozzle at this section

(3) The reaction of the jet issuing from the nozzle

(4) The mass discharge of the nozzle

From these data the values of the speed at the point considered were calculated —

(1) From equation (1) (= v_1 say)

(2) From the value of u/a given by equation VI and that of a calculated from the observed static pressure and the density calculated on the assumption of adiabatic expansion (= v_2)

The value of the mean speed (v_m) over the section of the outlet was also calculated from the reaction and the mass discharge.

The observations and reductions are given in Table IV

It will be seen that in the first two experiments the values of the calculated speeds at the axis of the nozzle are in good agreement with each other, and also the mean speed over the section is what would be expected from the comparatively slight retardation which is known to take place at the walls, *i e*, the mean values are 96 and 97 per cent of the speed at the axis Further, the pressure at the walls is appreciably lower than the pressure at the axis, as it should be. On the other hand, in experiment (3) the pressure at the walls is considerably higher than at the axis indicating the commencement of the breakdown of the motion and the values of the calculated speeds are *not* in approximate agreement It is clear, however, that the break away of the flow from the walls has not become considerable at this stage, since the mean speed is still of the same order as the calculated speeds. In the last experiment the break away is apparently complete and the disagreement between the calculated values of the speed is still more marked

The general conclusion from these experiments is that so long as a diverging nozzle runs full the flow may be taken to be sensibly adiabatic throughout except in the immediate neighbourhood of the walls

Section II —The Pressure and Velocity Distribution in High Speed Jets emerging into Still Air.

The characteristics of air jets emerging from a circular orifice into the atmosphere have been investigated by Emden* by means of the shadow method of Dvorak, in which a point source of light is used to throw a shadow of the jet on a screen On examination of the features of the shadow it was found that when the speed of the jet attained a definite value a series of bright equidistant discs became visible On increasing the air speed the distance between the discs increased and diagonal lines connecting their extremities

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* Wiedemann's 'Annalen,' Bd. 69, pp 264 and 426 (1899)

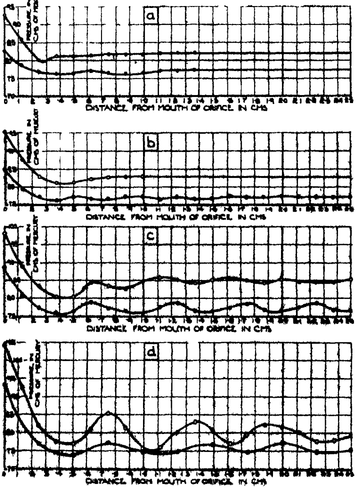
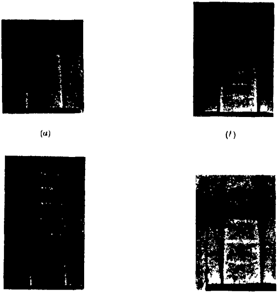


FIG. 11.—Pressure Distribution in Jets from No. 3 Orifice. Compare Plate 6, fig 12.
⊙ = along axis; • = along line parallel to axis and 0·51 cm. from it.
Initial Pressures in cms. of mercury *a* = 143·0; *b* = 147·7; *c* = 150·1; *d* = 157·3.

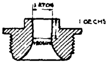


(*a*) (*b*)

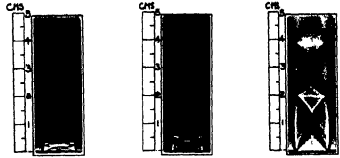
(*c*) (*d*)

Fig 12 Shadowgraphs of Jets from No 2 Orifice Compare fig 11
Initial Pressures in cms of mercury *a* 143 0 *b* 147 7 *c* 153 1 *d* 157 8

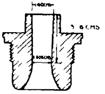
Fig 13 — Shadowgraph of Jet from No 2 Orifice Initial Pressure 225 cms
Compare fig 14



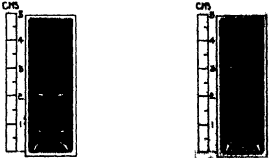
No 1



Initial Pressure 170 7 cms   Initial Pressure 185 4 cms   Initial Pressure 304 8 cms



No 2



Initial Pressure 235 7 cms   Initial Pressure 304 8 cms

Fig 15 Shadowgraphs of Jets discharged into the Atmosphere from Diverging Nozzles

([illegible])

also appeared. At still higher speeds the discs gradually broadened out into a wing shaped formation and the diagonals became curved These characteristics are illustrated in fig 12 in which is shown a series of shadowgraphs of jets from nozzle No 2 fig 2 at increasing speeds The discs were identified by Emden with stationary waves in the jet and their first appearance with the attainment of the velocity of sound in it but his conclusions that this velocity cannot be exceeded and that the pressure in the emergent jet is uniform and atmospheric have been shown by Lord Rayleigh to be erroneous [*]

A theory of the formation of stationary waves in jets has been developed by Prandtl [†] According to this theory the waves originate at the outer edge of the orifice and their characteristics will depend on the ratio of the pressure of the jet on emergence (p_1) to that of the atmosphere (p_2) If $p > p_2$ waves of rarefaction will proceed from the edge of the orifice inwards the velocity at any point being such that its component perpendicular to the direction of uniform density is that of sound at the temperature and pressure existing there It is also assumed that these waves of rarefaction will undergo reflection at the boundary of the jet and become waves of condensation On the other hand when the pressure on emergence is less than that of the atmosphere the initial disturbances are waves of compression which become waves of rarefaction from the boundary of the jet

The value of the wave length was deduced by Prandtl from the theory of the small disturbances in a cylindrical jet in which the motion is steady and under the assumptions of the existence at the boundary of atmospheric pressure and a discontinuity of velocity Taking the axis of y as that of the jet and assuming the velocity along the axis V to be nearly constant while u and w are small the solution of the equations of motion gives

$$v = \mathrm{V} + \mathrm{H} \cos \beta y \mathrm{J}_0 \left\{ \beta r \sqrt{\frac{\mathrm{V}^2}{a^2} - 1} \right\} \tag{8}$$

so that the wave length of the periodic features along the jet is given by $\lambda = \pi/\beta$

At the boundary of the jet since p is constant v is constant and therefore

$$\mathrm{J}_0 \left\{ \beta \mathrm{R} \sqrt{\frac{\mathrm{V}^2}{a^2} - 1} \right\} = 0 \tag{9}$$

The lowest root of this is 2 405 so that

$$\lambda = 2\ 61 \mathrm{R} \sqrt{\frac{\mathrm{V}^2}{a^2} - 1} \tag{10}$$

[*] Phil Mag vol 32, pp. 177 187 (1916)

[†] Physikalische Zeitschrift, p 599 (1904) and p 23 (1907)

In comparing the wave length given in this formula with the measured values obtained from photographs of the jet, which were somewhat similar to those shown in fig 12, Prandtl assumed that the values of V/a could be estimated with sufficient accuracy from the inclination to the axis of the jet, of the characteristic lines of the photograph indicating positions of maximum or minimum condensation and obtained what he considered to be a satisfactory check on the theory

For the purpose of the present investigation shadowgraphs of the jets emerging into the atmosphere from nozzles of different forms and at different initial pressures were obtained by the method described above and the interior of the jet was then explored by means of the static pressure and pitot tubes

These observations were sufficient to determine the length and amplitude of the stationary waves and the variations in the values of V/a along and at right angles to the axis

In the first series of tests the converging parallel nozzle No 2, fig 2 was used The variation of the static pressure was measured along the axis and also along a line parallel to it in the neighbourhood of the boundary for four different values of the initial pressure, and the results are shown plotted in figs 11 (*a*), (*b*), (*c*) and (*d*), the corresponding shadowgraphs are shown on Plate 6, fig 12 (*a*), (*b*), (*c*), (*d*) It will be seen that the amplitude and length of the waves diminish as the initial pressure is diminished, the disturbances eventually vanishing when the pressure in the jet on emergence exceeds the critical value $0\ 527\ p_0$

The results therefore confirm Emden's conclusions as to the nature of the motion, but definitely disprove his prediction of a uniform pressure and, as will be seen later of a velocity equal to that of sound throughout the jet. There is also a marked difference between the mean pressure at the axis and that in the neighbourhood of the boundary, and this difference is still considerable even when no wave formation is apparent

An interesting effect of this radial pressure gradient is that the velocity of sound is attained at the boundary before it is reached at the axis, and it would, therefore be expected that the waves would first be detected at the boundary In the case of (*a*), figs 11 and 12, this is seen to be the case

The corresponding values of V/a were calculated from the static pressure the pitot tube pressure observations by means of the Rayleigh formula, and are shown plotted in fig 14 for a higher value of the initial pressure

Comparing the observed distribution of pressure with the characteristic features of the shadowgraphs, it will be seen that the position of the discs corresponds with the sections of maximum condensation except in the case of (*a*) figs 11 and 12 where the variations of pressure although perceptible were too small to enable the outline of the wave to be determined with precision Further these positions also coincide with those at which the calculated value of V/a is unity which is a satisfactory explanation of the persistence of the disc effect even when the average velocity is considerably above the velocity of sound

It will be clear that this condition prevents any precise comparison of the observed wave length with the theoretical wave length obtained by Prandtl s investigation which assumes a constant value of V/a throughout the wave It may be remarked however that the observed wave length does correspond with a value of V/a intermediate between the maximum and minimum values attained Thus in the case illustrated in figs 13 and 14 the wave length is 1 4 cms so that the solution of equation (10) gives V/a = 1 33 The observed values of V/a throughout the wave ranged from 1 to 1 62

Shadowgraphs were also taken of jets discharged from diverging nozzles and these are illustrated in fig 15

In these cases it was possible by varying the initial pressure to make the emergent pressure of the jet either greater or less than atmospheric and so to vary the position relative to the mouth of the nozzle of the section of maximum condensation as will be seen from the shadowgraphs It will be seen that these shadowgraphs indicate the existence of a complicated series of waves proceeding from the interior of the nozzle in addition to those formed at the outer edges It would be anticipated from the work described in the preceding sections that the internal series of waves would disappear for a sufficiently high value of the initial pressure and this appears to have happened in the last experiments on nozzle No 1 In the case of No 2 nozzle the angle of divergence was too great for a waveless jet to be formed at the maximum initial pressure available

From the Prandtl theory of the formation of waves it might be supposed that in the case of a jet emerging into the atmosphere at a uniform pressure over its whole section equal to that of the atmosphere no waves would be detected even when the velocity was considerably above that of sound An attempt was made to verify this assumption by fitting a parallel portion to the end of a diverging nozzle and carefully watching the shadow of the jet on the screen while the issuing pressure as measured on the edge of the nozzle was gradually raised from a value below to a value above the atmospheric pressure This was repeated several times but no change in the wave pattern

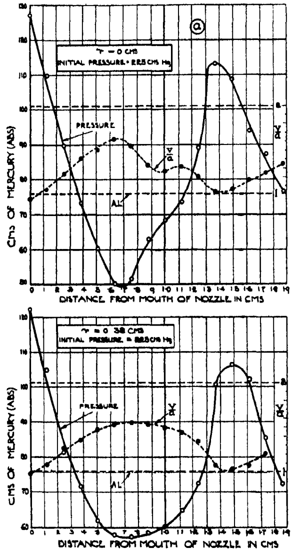


Fig. 14.—Pressure and Velocity Distribution Jet from No 2 Orifice discharging into Atmosphere Compare Plate 6, fig 13

could be detected in changing from a condition in which the atmospheric pressure was greater than that of the jet to one in which it was less It was concluded that the theory was inadequate to account for, at any rate, all the wave characteristics observed

The investigation was carried out in the Engineering Department of the National Physical Laboratory, and the author desires to acknowledge the valuable assistance of Mr R W Fenning in obtaining the shadowgraphs of the jets The author's thanks are also due to Mr A Eaton and Mr H Robinson, of the mechanical staff of the Department for assistance in making the experiments

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Tribo-Electricity and Friction

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(Communicated by Sir William Hardy, F R S —Received February 4, 1926)

I *Glass and Textiles*

This paper deals with the changes in the condition of glass surfaces when rubbed with flexible materials, chiefly cotton, linen, and silk, of varying purity The condition is ascertained by two different, but associated, properties —

- (*a*) The electric charges displayed by the glass surfaces when rubbed on textiles or on one another
- (*b*) The coefficient of friction found between two of them after being subjected to identical rubbing

We have derived great help in the friction work both as regards theory and technique from the papers on 'Boundary Lubrication," by Sir William Hardy and his colleague (1, 2, 3 4)

A solid surface may be modified in two distinct ways

(1) *By Addition of Material* —A solid surface exposed to an atmosphere containing water (or other) vapours, condenses and retains these, or if solid or liquid matter be rubbed on the surface, this will in general acquire and retain a covering film. The actual exposed surface is thus a complex of various materials, so that tribo-electric and frictional effects are complicated We know that the

friction of the surface is dependent on the character of the condensed film and on that of the solid underlying the film according to the expression given by Sir William Hardy and Miss I Doubleday (2)

$$\mu = b - aM$$

where M is the molecular weight of a condensed pure organic compound a and b being parameters

(2) *By Physical Change* Here a strain or orientation of the actual surface particles of the solid occurs

Sir G T Beilby (5) has shown that aggregation and flow on solid surfaces arise in certain conditions of rubbing or heating and result in unstrained and strained conditions respectively of the particles forming the outermost layers of the solid

At first sight it is incomprehensible that the rubbing of two seemingly identical bodies say two lengths of glass cut from a new rod should generate charges on the rods $+^{ve}$ on one $-^{ve}$ on the other But this effect was found and studied as long ago as 1765 by Bergman (6) Recently Rudge (7) has found similar effects for *like* bodies in the cases of quartz cinnabar mica sulphur oxalic acid and other materials It is easy to demonstrate these charges for like bodies in many other solids such as sealing wax ebonite or silk We shall attempt to show that effects of this kind in some cases following natural contamination are explainable by the principles (1) and (2) above

II *Tribo Electric Apparatus*

(1) The most convenient electroscope for observing charges is of the Hankel form in which a single gold leaf hangs vertically equidistant between two vertical parallel plates P P equally charged The leaf is so elevated that when highly charged its lower end lies over but cannot reach by 2 to 3 mm the plate to which it is attracted in this way we avoid the trouble of having to detach the leaf from a plate every time the former receives a large charge The plates are charged by a high tension battery of 100 volts one plate being connected to the $+^{ve}$ end the other to the $-^{ve}$ end the centre of the battery being earthed A wire from the head of the gold leaf passes to an insulated inductor I made of a short brass tube 2 inches in diameter (see fig 1)

The whole system is surrounded by an earthed metal case with a hole in one side through which charged rods can be introduced to the inductor without touching it The gold leaf is read by a microscope with micrometer scale of 100 divs, one scale division corresponding to about 1 volt potential of the leaf In special cases the sensitiveness is doubled

(2) From a length of soda-glass rod 4 mm. diameter, a number of lengths, each of 6 inches, are cut These rods are boiled all over in strong chromic acid for half an hour, then removed by tongs which have been cleaned in a blowpipe flame, they are rinsed well at the tap, then boiled in distilled water and finally stored in dry test tubes which have themselves been cleaned with chromic acid Throughout the cleansing the rods have touched tongs and inside of the test tubes, and no other solid Rods just cleaned as above we call " standard "

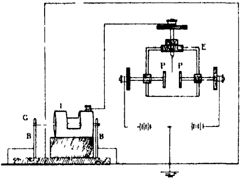

FIG 1 —The Electroscope, E, and Inductor, I

(3) The flexible solids used for rubbing are asbestos fibre, filter paper hemp fibre, yarn and fabrics of cotton, linen, silk, and wool The asbestos is as supplied purified by acids for chemical work It is handled with cotton gloves The filter paper is a smooth variety (Whatman, No 1) and in use a paper is taken fresh from the inside of the packet The textiles require long and careful cleansing, since even the best yarn or fabric obtained commercially is liable to be tainted with fats, waxes, pectins or resins natural to the fibres, whether vegetable or animal, as well as deposits from the air and soap or other dressings used in their manufacture The amount of wax in natural textile fibres is considerable In a recent paper by Lecomber and Propert (8), it is stated that in natural cotton the wax content is about 0 5 per cent Dr J V Eyre, Belfast, tells us that natural linen has 2 per cent wax, and many other impurities

In the first experiment to be described later, the fabrics we use are cleaned as follows —Boil with soap and soda for several minutes Then boil and stir in water repeatedly, and then wash for a long time in running water Extraction with purest benzene in a Soxhlet (having only clean *ground-glass joints*) for an hour is the next step The material is then dried Throughout the cleansing it is touched or moved only by tongs cleaned in a blowpipe or by a glass rod cleaned with chromic acid and then with water

(4) An electric stove is required to raise the glass on occasions to any temperature up to 300° This consists of a heating coil on a brass tube It is found that when glass rods are inserted into the tube without touching it they receive considerable charges due to combined induction from the considerable field in the heating coil and to conduction by the surface films *

So an earthed brass tube is placed inside the heating tube and a glass tube is inserted between the two brass ones Inside the earthed tube another glass one previously sealed at one end and boiled internally in chromic acid is inserted for cleanliness and to avoid any impurities likely to be given off by the hot brass A cleaned thermometer is placed in the innermost tube This heater of coaxial tubes quickly raises the rods to any desired temperature The inner glass tube is periodically cleansed

(5) In this kind of work it is necessary frequently to discharge a rod A small flame say 1 inch high is kept at hand When a charged rod is passed near to the side of but *not into* the flame most of the charge vanishes the residual charge can be made vanishingly small in a short time

III *Tribo Electric Experiments First Series*

Begin with two standard rods Call them A and B Take them from their test tubes by wrapping clean filter paper round one end to prevent contact with the hand Rub the free ends of the rods lightly together The friction between them is great but the electroscope shows that no charges arise on them We may therefore consider their surfaces physically and chemically identical Warm the working end of A in the heater for a few seconds Then rub the rods together The electroscope now reveals a $-^{ve}$ charge on A (see fig 2 col 1) Next warm B and rub on A B becomes $-^{ve}$ Therefore charge on A is now $+^{ve}$ (see col 2)

This process of warming one rod and so rendering it $-^{ve}$ to the other can be repeated indefinitely unless in the process both rods rise to about 200°

On allowing both rods to cool thoroughly and then rubbing them together, no charge arises Hence the warming processes have not permanently affected them The curve returns to the base line ZZ′ (see col 3)

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* When one end of a glass, ebonite or other insulating rod is held by hand for a few seconds near a wire carrying a current in a 200 volt circuit the field induces charges on the rod and the films on the rod discharge through the hand the charges repelled from the field Thus the rod receives a charge easily detected by the electroscope. The experiment of course fails for a good conductor or for a very clean insulator but glass ebonite and sealing wax as usually found, show this effect

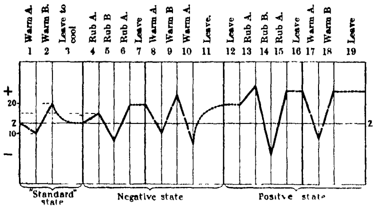

FIG 2 shows the sign of the charge (ordinates) on rod A relative to rod B as they are treated to differential heating or rubbing and then rubbed on one another Abscissæ represent progress in the experiment as the glass passes from standard state at Z to a much rubbed state at Z′ *Broken* line shows *warming* *dotted* line shows *leaving* *full* line shows *rubbing*

Rub A lightly with silk purified as in section II

A acquires a $-^{ve}$ charge against the silk

Discharge A and rub it on B It becomes $+^{ve}$ (col 4)

Discharge A and B and rub B well on the silk B becomes $-^{ve}$

Discharge B and rub against A A receives a $-^{ve}$ charge (col 5)

Discharge A and B and rub A well with the silk It becomes $-^{ve}$ (col 6)

A has now been rubbed with silk more than B and is therefore $+^{ve}$ to it It will remain so as long as both rods are left intact (col 7)

Warming A and B alternately, we obtain, as in columns 8, 9, 10, 11, the same effects due to heating as we found in columns 1 2 3 before any rubbing had been performed, but with this difference, that when both are cold the $+^{ve}$ state of A caused by rubbing in col 6 remains at the end of col 11

Rub A hard with silk At first A is $-^{ve}$, but ultimately it becomes $+^{ve}$

Discharge A and rub it on B A becomes $+^{ve}$ (col 13)

Discharge A and B Rub B hard on the silk B at first is $-^{ve}$ but ultimately becomes $+^{ve}$ If the rubbing process has gone far enough, B will now be found $+^{ve}$ to A, i e A is $-^{ve}$ (col 14) A is again brought $+^{ve}$ to B by prolonged rubbing on silk (col 15)

In this way the rods can be made alternately $+^{ve}$, one to the other But there is an asymptotic limit beyond which neither can be brought Then the polish on each is complete

Warming first one rod and then the other, we find the same temporary effects (cols 17 and 18) as previously in cols 1, 2, and 8, 9, 10 There is a further instance of reversibility due to heating a rod which is slightly $+^{ve}$ to silk will, on warming, become $-^{ve}$ to it

It will be seen from the above that whether glass is in (1) "standard" state, or (2) $-^{ve}$ state to silk, or (3) $+^{ve}$ state to silk, the effects of heat to make it more $-^{ve}$, or of rubbing with silk to make it more $+^{ve}$, are identical The change from glass $-^{ve}$/silk $+^{ve}$, to glass $+^{ve}$/ silk $-^{ve}$, which occurs at a certain stage in the above rubbing is shown at B in curve 2, fig 3

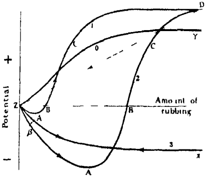

FIG 3 —Curves, 0, 1, 2, 3 show respectively the nature of charge $+^{ve}$ or $-^{ve}$ on glass, as rubbed by textiles of various grades of cleanliness commencing with the least clean The glass at point Z is in "standard" state

Next perform the above experiments on standard glass rods using, one at a time, in place of silk, the other textile materials— hemp, jute, cotton, linen, wool The effects throughout are identical in kind with those found when silk was used, though some materials such as silk or wool rub up large charges more readily than, say, hemp or jute

When, however, the experiment is performed with asbestos fibre and filter paper, it is found impossible to bring up a polish on the glass or, by prolonged rubbing, to make it $+^{ve}$ to silk or wool Otherwise the effects are identical with those obtained above Thus, when a rod, say A, is rubbed with the asbestos fibre, it becomes $-^{ve}$ to the asbestos and $+^{ve}$ to B When B is now rubbed with asbestos it becomes $-^{ve}$ to the asbestos and $+^{ve}$ to A Again, warming rod A or B depresses it so that it becomes $-^{ve}$ to the other rod Unlike the textile materials continued rubbing by asbestos fails to bring up polish on the rods in fact, the surface becomes abraded

With filter paper the glass is not visibly abraded but its fibres are torn up by the rough glass and it will not produce polish Further if a polished glass which is $+^{ve}$ to silk be rubbed by filter paper it at once loses its polish *i e* feels rough to the paper and charges $-^{ve}$ to filter paper and to silk In interpreting these experiments we have to account for four distinct effects

(*a*) The $-^{ve}$ effect of rise of temperature is general It is found alike on clean glass and on glass whether in $-^{ve}$ or $+^{ve}$ state due to rubbing with the textiles It is therefore not a property purely of a clean glass surface or of a film surface but of something common to both We know that water from the air is quickly adsorbed on glass surfaces whether clean or filmed Again we know (9) that a water film when broken by impact of air receives a $+^{ve}$ charge It may be that when a hot dry rod rubs a cold damper one the water film on the latter is broken and becomes $+^{ve}$ as in our experiments and the drier rod becomes $-^{ve}$ This explanation meets all the above cases for when both rods are well warmed and water films driven off the effect ceases

(*b*) The charges on the glass due to rubbing with silk or other textile are at first $-^{ve}$ but later become $+^{ve}$ and this is the final condition persisting however long rubbing continues and however much the textile surfaces are renewed

(*c*) Concurrently with its change in tribo electric character the glass shows decreasing friction against the rubber and attains a polish

(*d*) If two glass rods are rubbed together that one is $+^{ve}$ which has been rubbed most by the textile

The effects (*b*) (*c*) and (*d*) unlike (*a*) are *permanent* and indicate a chemical and/or physical change of surface on the glass To account for this permanent change we have at hand the theory of Sir William Hardy and Miss Doubleday (*loc cit*) according to which the glass starting clean would acquire from the textile a film of organic impurities wax fat etc still clinging to the cellulose or ceratin after cleansing Pursuing this film argument we suggest that while the final $+^{ve}$ charge found clearly indicates the presence of a complete primary film, the initial $-^{ve}$ charge is evidence of no film or of one so thin that the underlying glass has a preponderating $-^{ve}$ influence We are on this supposition, getting for the $-^{ve}$ state (fig 2) a textile/glass and not a textile wax effect

When wax is transferred from silk to glass a shearing process occurs in the wax, some still remaining on the silk. This shearing occurs, as it generally does, sometimes between molecules and sometimes within the molecules, so that electrical separation occurs $+^{\text{ve}}$ going to the silk side, $-^{\text{ve}}$ to the glass side. This would account for the initial $-^{\text{ve}}$ state of the glass on the supposition that when wax is passing from silk to glass the charges arising are glass $-^{\text{ve}}$, silk $+^{\text{ve}}$.

As rubbing continues equilibrium arises when the glass surface tending to wax saturation and the silk to wax exhaustion the wax is pulled equally across the interface. Reversal of sign now occurs, the glass receiving a $+^{\text{ve}}$ charge. But since both surfaces now have a wax layer, the electrical separation (which only occurs for unlike surfaces) must be attributed to the differential influence of the underlying glass and silk, operating through the wax layers. We have authority for this view in what Sir William Hardy and Miss Doubleday (2) call an "irradiation of force" acting from the underlying solid through a film and represented by the parameter b in the formula already quoted $\mu = b - aM$.

It will be seen that this general explanation accounts for effects (*b*) and (*d*) equally well. As for the effect (*c*), the accumulation of wax well rubbed on will necessarily lower friction.

IV *Tribo-Electric Experiments. Second Series.*

Not being satisfied that the residual impurities of the rubbers had been removed to the limit, we exhausted the cotton, linen, and silk in the Soxhlet for a further 15 hours in extra pure benzene. The result fulfilled our hopes. All the three textiles now set up $-^{\text{ve}}$ charges on the glass indefinitely, $+^{\text{ve}}$ charge in no case arising even after 15 minutes rubbing. Fifteen hours treatment in the Soxhlet with tri-chlorethylene produced no perceptible further effect on the tribo-electric character of the textiles, though, in the case of cotton, it disintegrated to rottenness. In the curves 2 and 3, fig. 3, we see the effects of partial and thorough cleansing.

Thus at last we have so far purified the textiles that they have very little residual wax, and glass when rubbed by them retains its pristine $-^{\text{ve}}$ tribo-electric character.

Having hitherto employed fabrics (which are complicated with warp and weft) we next turn to yarns. In this case all the fibres are parallel to one another and our problem is rendered easier. When a rod has been rubbed for some time and is near the critical condition (see section VI) it rubs $+^{\text{ve}}$ along fibres, say of jute or hemp, but rubs $-^{\text{ve}}$ across the fibres. Further rubbing either way leads ultimately to $+^{ve}$ Clearly then yarn is preferable to fabric for our purposes for we can ensure that in rubbing the action is either along or across the fibre

The yarns were wrapped on standard glass rods and cleansed in the same drastic fashion as the fabrics (see section II) We found that their tribo electric behaviour with respect to glass is identical with that of fabrics when impure they render glass finally $+^{ve}$ when pure $-^{ve}$ As a further generalisation of our results we find it is immaterial whether soda glass lead glass or vitreous silica is used We conclude that all members of the glass family react as above to any of the textiles—cotton linen and silk

V *Friction Experiments*

To ascertain the coefficient of friction (μ) of two glass rods at any stage in the rubbing we use a tilting apparatus One rod *a* shown in section fig 4 is supported horizontally on two brass plates one of which is shown at X *a* is held

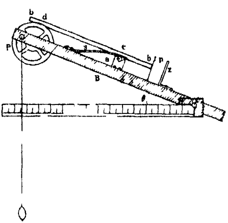

FIG 4 —The Friction Apparatus. Rod *bb* begins to slip on rod *a* for an angle of tilt θ

in place by spring S The other rod *bb* rests on frictionless pulley P at *d* and on rod *a* at *e* The pulley and brass plates are mounted on a board B and when this is tilted on a horizontal axis O rod *bb* *begins to* slide on *a* for a critical angle of tilt θ Working out the reactions we have $\mu = K \tan \theta$ where K is a constant depending on the positions of *d* and *e* relative to the centre of *bb* It is clearly essential always to have *bb* starting at one place in the apparatus since K depends on this. The end *b* of the rod is for this reason placed in the line joining two pins, one of which is seen at p. Z is a stop to prevent b going far The rods are moved to and from this apparatus by clean tongs and bear on one another at those ends which have been rubbed

Standard glass rods (see section II), if tested directly after cleansing, have a high value of μ For soda glass, which we generally use, this value is about 1·2 with variation of 20 per cent both up and down This variation from place to place, round the circumference of the rod, must be due to irregularity in the nature of the glass, for if we keep to one generating line of the rod μ is constant. There seems to be streakiness running along the length of the rod due to unequal composition of material taken from the pot in manufacture When the glass has received a film by adsorption from the air or by material received from the rubber, this film attains uniformity and the streakiness disappears

The vitreous silica we have used has, when in " standard " state, a lower value of $\mu = 0·94$

The curves in fig 5 show that glass slowly loses its " standard " quality if left exposed to ordinary air Hence our practice is to rub the rods as soon as possible after cleansing The curves show that μ falls farther in one hour in cold, damp outdoor air (in December) than in one day in the warm, drier air of a laboratory, although we should expect the air in the former case to be more free of dust and condensable vapours, other than water

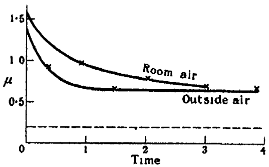

FIG 5 —Gradual fall in mutual friction for rods, commencing " standard," as exposed to air contamination Time units are days for room air curve : hours for outside air curve

VI

The value of μ, which falls slowly in air, does so rapidly if rubbed by the textiles. This can be shown in a systematic way by wrapping the textile yarn or fabric on a clean rod and pressing this with a definite force on the standard rod, which is rotated on its length at speed varying from 500 to 2,000 revs per minute by a motor In fig 1 the glass rod G is supported by two plates B, B, into which it fits. A motor shaft, not shown, can be joined to the left end of G The textile mounted on the rod for rubbing is pressed by a known weight on the glass through the gap shown in I We have, then, two independent variables — (*a*) The pressure between the surfaces, (*b*) the time of rubbing In fig 6 the curves show that in 10 seconds of rubbing ordinary flannel reduces μ to 0 25, and other ordinary textiles behave in like manner as shown In all these cases the change from $-^{ve}$ to $+^{ve}$ charge on the glass occurs for a value of μ about 0·18 This critical value of μ is shown by the horizontal dotted line The curves 4 and 5 in fig. 6 show the relation μ/t for the cleanest textiles, the load being 200 gms In half a minute at this high pressure μ is lowered to only 0 62 Further rubbing causes no steady reduction in μ, but we find a small erratic *up* or *down* value which we cannot attribute to errors in measurement To account for this apparent caprice we tried the effect of rubbing the rods either (*a*) at one spot of the wrapped textile or (*b*) with frequent change of the surface of the textile The results shown in fig 7, the pressure applied being again 200 gms throughout, provide the explanation we are seeking When the rub occurs at one spot of the textile, as during stages B and D, μ rises even to value 1 0. When, however, the textile surface is renewed during the rub, as during stages A and C, μ descends to a low value. In the light of the work of Sir William Hardy and Miss Doubleday, the explanation seems clear Heat is generated by prolonged rubbing with the great pressure used When the heat is concentrated at one spot of the textile, its surface becomes so hot that the lubricant (wax)

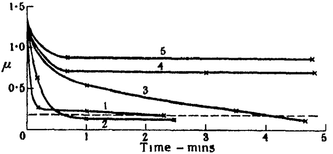

FIG. 6.—Change in friction for standard rods when rubbed with (1) ordinary flannel, (2) ordinary hose, (3) ordinary silk, (4) very clean linen yarn, (5) very clean cotton fabric

becomes fluid and the textile absorbs it Thus the glass beneath is exposed to direct rubbing by the textile, with resultant high value of μ. Messrs. Lecomber

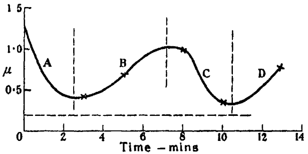

Fig. 7 —Variation in mutual friction of glass rods according as the textile used on them has (A and C) or has not (B and D) been freely moved during the rubbing

and Propert (*loc cit*) show that cotton waxes melt at about 80° C Such a temperature might easily be attained for sustained large pressure at one spot When, on the other hand, fresh cool surfaces of the textile are used, temperature rises much less and the lubricant remains solid The authors "On Boundary Lubrication" quoted above showed that a fluid lubricant can be rubbed away from a surface, but that rubbing a solid lubricant does not entirely remove it, but improves its polish, until it is probably reduced to monomolecular thickness

On these lines it seems possible to explain the anomalous tribo-electric behaviour of textiles on solids. It is often found that a hard rub makes the solid $-^{\text{ve}}$, but a light rub, or flick, renders it $+^{\text{ve}}$. This occurs when the solid surface has acquired a certain degree or condition of film. As we have seen above, the value of $\mu = 0 \cdot 18$ is critical Glass rubs $+^{\text{ve}}$ for less value of μ, and $-^{\text{ve}}$ for greater values. If, then, the glass surface is near this critical state, we can attain $+^{\text{ve}}$ or $-^{\text{ve}}$ according as pressure is light or heavy.

VII.

We have assumed hitherto that our cleaned textile material still contains enough wax to cause the lowering in μ, seen in curves 4 and 5, fig. 6 This is a simple *film theory*. But we must not forget the claims of a *strain* theory Standard glass surfaces are made by long-continued boiling with chromic acid at 130° C The acid not only removes impurities, but also attacks the glass surface, and so loosens the particles as to give opportunities for orientation, *i.e.* relaxation from strain When this standard glass is rubbed, orientation is destroyed and strain is set up, as Beilby's work shows Burdon (10) shows that dilute HCL spreading over clean mercury attacks only one-tenth of the atoms of the surface, supposing the full density (13 6) remains up to the geometrical surface If, however, *all* the mercury atoms on the surface are attacked, the density of the mercury can only be 1 36 We see from this the possibility that free surfaces (even glass after surface agitation) may have peculiar structure, easy to destroy by violence, such as rubbings The surface would then attain a state of strain

It seems probable that in our experiments both effects (film and strain) play a part, and that the strain effects may become relatively important when the applied pressure is great and the residual impurity on the textile is small We have rubbed standard glass with clean filter paper and clean glass-wool as well as with the very cleanest textiles In *all* cases the value of μ falls to values 0 86 to 0 90 Now this lowered value (which is yet far above those due to impure textiles) cannot be attributed to residual impurity common to all the rubbers, as these are so diverse in constitution, unless the impurity in the case of each of them is derived from the air This we know is not the case for recently cleaned material

To test whether μ is ever lowered in the absence of film, we tried a crucial test Prepare three standard glass rods A, B, C Measure μ for B and C Rub A first on B, then on C for half a minute, using the motor device of section VI, and rubbing very lightly Find μ again for B and C The value of μ was 1·23 before rubbing, 0 99 after rubbing, so that mere pressure on a surface *without the possibility of film formation* causes a reduction of μ The rubbing rendered the surfaces matt, and it might be argued that the reduction in μ is not due to strain but to a change in the form of the surface from the polished to the rough appearance. We next cleansed these matt rods with chromic acid in the usual way and re-tested for μ We found that it recovered hardly at all, being 1·0. It is, therefore, clear that film is not the only cause of reduction in μ.

VIII

Something must now be said as to the actual purity of the cleansed textile materials, since any effect on the friction of glass caused by rubbing with very pure textiles might be due to strain rather than to film We have received much advice as well as specially purified material from Dr L Balls and Mr. F P. Slater, Fine Cotton Spinners Association, Manchester, from Dr J. V. Eyre, Linen Industry Research Association, from Mr J. W Windley, Silk Merchant, Nottingham, and from others. We acknowledge gratefully all this help. In some cases, notably the linen from Dr Eyre, the purification took over a month and involved numerous acid, alkaline and bleaching processes. We found that all these prepared fabrics and yarns rub glass $-^{ve}$ but never $+^{ve}$. They all lower the coefficient of friction of standard glass to about 0·6. After exhausting them with benzene and chloroform on a Soxhlet, and then rubbing on the glass, the glass friction is lowered to less extent than before. This improvement may be attributed to the removal of natural contamination settling on them in the course of days or weeks since purification.

Some students of cellulose and other organic fibres have doubted the possibility of so far cleansing these materials of wax that not even enough will remain to yield a monomolecular layer on any solid on which they are rubbed. Even if the *surface* of the fibres were absolutely cleansed by the benzene or other solvent, the standard glass, having a surface of high friction, would grind into the wall of the fibre and take up residual wax from inside the fibre, where the solvent had been unable to operate fully. If this be so, we could not expect to get a fibre really free of wax short of disintegrating it into the smallest particles. It would thus be a vain hope to expect to get a really pure textile, however far the cleansing were pursued.

As to the very pure commercial solvents we used, all when evaporated down left first a small amount of residual thick oil and, finally, when dry a perceptible powder. Correspondingly we found these solvents all lowered the coefficient of friction of glass when this had been dipped in them and dried. The benzene reduced μ by 0·33, the other solvents by 0·27 and 0·13. Another indication of pollution is that the residue changed the tribo-electric character of standard glass. We have thus three lines of evidence all showing that these solvents are untrustworthy. Yet the distillate from them in the Soxhlet is of high purity. This is shown by placing standard glass rods in the Soxhlet and boiling for 15 minutes. On testing the rods for friction before and after the process, the value of μ remained constant at 1·24. We thus obtained such pure solvents by the Soxhlet that it is questionable whether solvents of a higher grade than these commercially "pure" ones will prove more effective in reducing residual wax on the textiles.

IX

We have seen that the value of μ for standard glass falls when it is left in air or when rubbed by a variety of flexible bodies. We now notice some cases in which the reverse process occurs. Suppose μ for glass has been reduced by rubbing to the low limiting value 0·13. There are three ways in which this value will be found to rise (see fig 8) · —(*a*) Leaving in ordinary air. The rise in μ is slow, but in five days it rises to 0·54. (*b*) In vacuum (0·001 mm). In five minutes μ rises to 0·21. (*c*) Heating to a high temperature (220° C). In a very short time μ rises to 0·51.

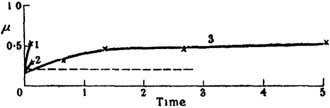

FIG 8 —The curves show how glass rods after being well rubbed with impure textiles recover a measure of friction, when heated (1), or in vacuum (2), or when left in air (3). Time units are hours for curves 1 and 2; days for curve 3.

To account for the rise in μ in these three diverse cases, we might expect heat and perhaps vacuum to reduce some of the solid film formed by the rubbing. But we should not expect the *film* to escape from the surface when left in air, for we know from section V that the reverse process occurs. On the other hand, any *strain* imposed on the film in rubbing would be relaxed quickly by heat, slowly by vacuum, and very slowly when left in the air by the thermal agitation of the glass below the film and by the incessant bombardment and adsorption of gases from the air.

The facts just quoted correspond with experience in tribo-electricity. For we find that when glass by rubbing has been rendered $+^{ve}$ to silk, it will be found to reverse to $-^{ve}$ if (*a*) left in air for many hours, (*b*) left in vacuum for several minutes, or (*c*) heated to 220° for a few seconds.

In each case the dotted line (*i e* the critical state) is crossed (*see* fig 8), as one of us has shown (*c*) in previous papers (11, 12). Reversal of sign occurs, as we have seen (section VI), for a critical value of μ about 0·18 (see dotted line, fig 8).

We have already found that the effect of ordinary air on *standard* glass is to lower μ to a medium value, say 0·6. Now we find it raises μ for *polished* glass to about 0·5. Thus, however glass be treated, it settles in air to a medium condition with $\mu = 0·5$ to $0·6$.

X. *Conclusion*

The method in most tribo-electric experiments in the past has consisted in observing charges arising by rubbing together two solids of different composition. Surface conditions are highly complex, physically and chemically, so that such experiments have, in general, led to indefinite results. It is a case of one equation with several "unknowns."

Our method is to combine such experiments as the above with those of two other kinds:—

(*a*) Observation of the charges arising by rubbing together two like solids—in this case glass/glass—which have been rubbed or heated differently.

(*b*) Observation of the mutual friction of two like solids—here glass/glass—which have been similarly rubbed or otherwise treated in a systematic way.

We have thus three points of view, and we have found a stereoscopic method, such as this, fruitful in results. We are continuing it with solids other than glass and textiles. It is clear that solid films play a great part in our experiments. How far orientation and strain at the interface may influence results remains to be seen.

The following definite effects have been found:—

(1) A glass surface starting in a standard state of purity adsorbs condensable material if left in the air and its coefficient of friction (μ) *slowly* descends in several days from some high value, say 1·2 to about 0·7.

(2) Ordinary textile materials when rubbed on the standard glass bring about the lowering of μ *quickly*. Continued rubbing will bring down even as low as 0·13. For a value of $\mu = 0{\cdot}18$ the charge on the glass due to rubbing becomes $+^{ve}$, having been $-^{ve}$ for higher values of μ.

(3) Textile materials, rendered very clean by prolonged treatment with solvents (benzene, etc.), slowly reduce μ for the glass on which they are rubbed to about 0·6, as the limit. The friction never descends to 0·18 and the glass remains $-^{ve}$ and never acquires a $+^{ve}$ charge.

(4) When a glass surface has attained a very low value of μ, say 0·13, it acquires a higher value (even 0·54) when heated, or placed in a vacuum, or left in air.

(5) When glass has medium values of μ, the sign of the charge due to rubbing can be made $+^{ve}$ or $-^{ve}$ according as the rubbing is gentle or violent, and when the yarns and fabrics are used, according as the rubbing is along or across the fibre.

(6) Two standard glass surfaces acquire no charges when rubbed together, but if one has been rubbed by a textile more than the other it is $+^{ve}$ to the other.

(7) If one of two identical surfaces of glass be heated and then rubbed on the other, it becomes $-^{ve}$ to it.

REFERENCES

(1) Sir W B Hardy and Miss I. Doubleday, 'Roy Soc Proc,' A, vol. 84, p 220 (1911).
(2) Sir W B Hardy and Miss I. Doubleday, 'Roy Soc Proc,' A, vol. 100, p 561 (1922).
(3) Sir W B Hardy and Miss I Doubleday, 'Roy Soc. Proc.,' A, vol 101, p. 487 (1922)
(4) Sir W B Hardy and Miss I Doubleday, 'Roy Soc. Proc,' A, vol. 108, p. 22 (1925)
(5) Sir G T Beilby, 'Aggregation and Flow of Solids,' MacMillan and Co
(6) Bergman (see Riess's 'Riebungs-electricität'), pub 1853
(7) W A. D Rudge, 'Roy Soc Proc., A, vol 90, p 256 (1914)
(8) L. V. Lecomber and M. E Propert, 'Shirley Institute Memoirs,' Didsbury, October, 1925
(9) H W Gilbert and P E Shaw, 'Proc Phys Soc,' vol 37, June, 1925
(10) R S Burdon, 'Proc Phys. Soc,' December, 1925
(11) P. E. Shaw, 'Proc Phys Soc.,' April, 1915
(12) P E. Shaw, 'Roy Soc Proc,' A, vol 94, p 16 (1918)

The Absorption Spectra of some Naphthalene Derivatives in Vapour and Solution

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Having examined the absorption spectra of naphthalene* and its methyl† derivatives, I have continued the investigation in order to see how the spectrum of naphthalene is affected by the introduction of different groups in the alpha and beta positions

The technique employed for the solution‡ and vapour* spectra has been fully described elsewhere Pure hexane§ was used as a solvent unless otherwise stated ϵ is the molecular absorption coefficient The substances were purified by crystallisation from hexane Liquids were fractionally distilled *in vacuo*

The absorption curve of naphthalene consists of two parts Part I contains 9 sharp bands A-L between λ 3207 (ϵ 16) and λ 2930 (ϵ 365) Bands C (λ 3110) and H (λ 2975) are very strong and have an interval of 1460 cm^{-1}. This interval repeats itself in most of the mononaphthalene derivatives, particularly in the case of the beta bodies. There is also a smaller interval D-C of 451 cm.$^{-1}$ and L-F 2 × 453 cm $^{-1}$ At λ 2700 the curve goes up steeply from ε 365 to ε 4800 Here starts Part II, which consists of 8 bands 1-8 These are much broader and more diffuse than those of Part I In all the bodies examined in this paper these two well-marked sections in the spectra are found, hence the use of the expressions Parts I and II will be continued

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* V. Henri and H. de Laszlo, 'Roy Soc. Proc.,' A, vol. 105, p 662 (1924)

† H. de Laszlo, 'Comptes Rendus,' vol. 180, p. 203 (1925)

‡ V. Henri, 'Etudes de Photochemie' (1919).

§ V. Henri and A. Castille, 'Bul. Soc. Chim. Biol.,' vol. 6, p. 299

The *Bromonaphthalenes*, α boiled at 279° C, (735 mm) and β was obtained as white scales m p 57° C The solution-spectra in hexane (see Table I and fig 1)

TABLE I —Solution Spectra of

α-Bromonapthalene and β-Bromonaphthalene in hexane.

Band	λ	1/λ	ε	Band	λ	1/λ	ε
Part I				Part I.			
I	3216	31090	140	A	3220	31060	265
II	3157	31680	345	B	3168	31570	125
III	3107	32190	460	C	3143	31820	185
IV	3053	32750	870	D	3118	32070	220
V	3016	33160	1350	E	3074	32530	275
				F	3010	33220	250
Part II				Part II			
VI	2987 2972 2957	33480 33650 33820	3450	G	2909 2897 2885	34380 34520 34660	2300
VII	2924 2914 2904	34200 34320 34440	3400	L	2800 2781 2763	35710 35960 36190	3300
VIII	2882 2852 2822	34700 35060 35440	4800	O	2689 2675 2662	37190 37380 37570	3150
X	2769 2744 2719	36110 36440 36780	4350	S	2610 2602 2595	38310 38430 38540	3000
XII	2662 2646 2630	37570 37790 38020	3450	T	2579 2575 2571	38770 38830 38900	2750
				R	2531 2517 2504	39510 39730 39940	2300

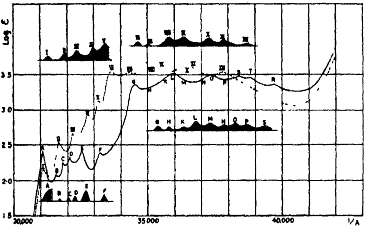

FIG 1 —Bromonaphthalene in Hexane.

α Bromonaphthalene	I V, $t = 120°$, VI VIII, $t = 50°$
β-Bromonaphthalene	A F, $t = 130°$, G-S $t = 60$.

are very like those of the methyl naphthalenes * α-Bromonaphthalene has a big period of II-V = 1480 cm $^{-1}$ The following intervals also occur —I III = 1100 cm $^{-1}$, II-IV = 1070 cm $^{-1}$, and III-V = 1070 cm $^{-1}$. These probably represent a true interval of about 540 cm $^{-1}$ The β body has an interval of 1470 cm $^{-1}$ The following periodicities also appear B-D = 500 cm $^{-1}$, and A-B = 510 cm $^{-1}$ giving an average of 505 cm $^{-1}$. The vapour bands (see Table II and fig 1) of the isomers reproduce the solution bands with regard to their relative positions and intensities Band A has a definite fine structure, which will be investigated later with a modified light source

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* H. de Laszlo, 'Z f. Phys. Chem.,' vol. 118, p. 370 (1925); and 'Comptes Rendus,'

TABLE II.—Vapour Spectra of

α-Bromonaphthalene. and β-Bromonaphthalene.

Band	λ	1/λ	Band.	λ	1/λ
	Part I at 120° C			Part I at 130° C	
I	3210 3182	31150 31430	A	3223 3195,1 3192,6 3188,1 3183,4 3182,5	31030 31298 31322 31367 31413 31422
II	3157 3124	31680 32010	B	3155 3151	31700 31740
III	3100 3085	32260 32410	C	3126 3117	31990 32080
IV	3036 3026	32940 33050	D	3106 3091	32200 32350
V	3000 2985	33330 33500	E	3076 3045	32510 32840
			F	3006 2990	33240 33440
	Part II at 50° C			Part II at 60° C	
VI	2900 2857	34480 34780	G	2838 2815	35240 35520
VII	2859 28590	34960 35060	H	2800 2783	35710 35930
VIII	2800 27840	35710 35920	K	2763 2740	36190 36500
IX	2760 2739	36230 36510	L	2725 2709	36700 36910
X	2690 2675	37170 37380	M	2689 2672	37190 37430
XI	2651 2637	37720 37990	N	2652 2632	37710 37990
XII	2592 2575	38580 38830	O	2621 2609	38150 38330
			P	2592 2571	38580 38900
			S	2547 2531	39260 39510

The *Chloronaphthalenes.*—α boiled at 258° C. (740 mm.) and β was crystallised from 80 per cent. ethyl alcohol and melted at 58° C. In the solution-spectra in hexane (see Table III and fig. 2), the relative positions of the bands of both chloro compounds are the same as those of the corresponding bromo derivatives The band heads of the latter are shifted towards the red in comparison with those of the former by the following amounts Part I of α bromonaphthalene 50 cm $^{-1}$ Part II, 90 cm $^{-1}$, Part I of β bromonaphthalene, 70 cm $^{-1}$ Part II, 105 cm $^{-1}$

TABLE III —Solution Spectra of

α-Chloronaphthalene in Hexane and β-Chloronaphthalene in Hexane

Band	λ	1/λ	ε	Band	λ	1/λ	ε
	Part I				Part I		
I_A	3242	30845	76	A	3212	31130	400
I_B	3199	31260	200	B	3161	31640	145
II	3153	31720	380	C	3136	31890	220
III	3102	32240	515	D	3111	32140	350
IV	3048	32810	1000	E	3068	32590	4200
V	3011	33210	1480	F	3004	33290	350
	Part II				Part II.		
VI	2981 2963 2945	33550 33750 33960	3800	G	2900 2888 2876	34480 34630 34770	3050
VII	2917 2909 2900	34280 34380 34480	3800	L	2788 2774 2761	35870 36052 36220	4000
VIII	2864 2844 2824	34920 35160 35410	5150	O	2679 2668 2657	37330 37480 37640	3700
IX	2758 2738 2719	36260 36520 36780	4800	S	2604 2595 2585	38400 38540 38680	3450
X	2660 2640 2620	37590 37880 38170	3800	T	2573 2569 2564	38870 38930 39000	3300
				R	2525 2510 2495	39600 39840 40080	2750

Band I of α-bromo- is resolved into two in the case of α-chloronaphthalene We conclude therefore that the introduction of a halogen atom into a ring body disturbs the character of the latter's absorption spectrum but little, the whole being shifted towards the red, the amount of this shift being dependent upon the atomic weight of the substituting atom

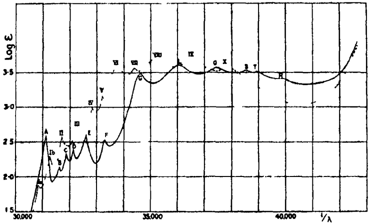

FIG 2 —Chloronaphthalene in Hexane

Broken line α-Chloronaphthalene, solid line β-Chloronaphthalene

The cathodoluminescence spectra of the bromonaphthalenes were examined by Goldstein * This bears out our theory of the production of absorption and emission bands †

The Naphthols —α Naphthol melted at 94° C and β at 123° C The solution spectra in hexane are shown on fig 3 and Table IV The average intensity of the two curves is about four times that of naphthalene the small bands being well marked The action of the —OH group on the naphthalene spectrum is comparable to its action on the benzene spectrum ‡ The phenol solution spectrum in hexane consists of three very prominent bands whose average intensity is about five times that of the benzene spectrum the whole being shifted 2220 cm $^{-1}$ towards the visible We note the following frequency intervals between the various bands —α Naphthol I V, 1470 cm $^{-1}$ IV VII, 1470 cm $^{-1}$, average, 1470 cm $^{-1}$ β Naphthol B E, 1380 cm $^{-1}$, C G, 1460 cm $^{-1}$ D-H, 1430 cm $^{-1}$ E I 1400 cm $^{-1}$, average, 1420 cm $^{-1}$ These intervals differ but little from that of naphthalene

* 'Verh d D Phys Ges,' vol. 6, p 161 (1904)

† 'Z f Phys Chem,' vol 118, p 395 '

‡ Klingstedt, 'C R. vol. 174, p 812 (1922)

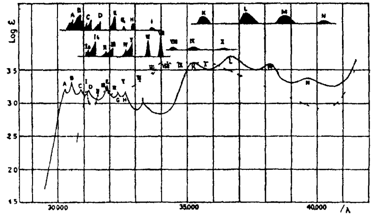

FIG 3 —Naphthol in Hexane

α Naphthol	A I $t = 115$ K N $t = 90$
β Naphthol	I VII $t = 100$, VIII X $t = 75$

TABLE IVA —Solution Spectrum of α Naphthol

In Hexane				*In Ethyl Alcohol*			
Band	λ	1/λ	ε	Band	λ	1/λ	ε
			Part I				
I	3215	31100	1820	I	3237	30890	1900
II	3170	31550	1380				
III	3139	31860	1740	III	3163	31620	1750
IV	3106	32200	1500				
V	3070	32570	1820	V	3093	32330	2000
VI	3014	33180	2200	VI + VII	3022	33090	3300
VII	2970	33670	2900				
			Part II				
VIII	2951 2924	33890 34200	4300				
IX	2890 2867	34600 34880	4300	VIII+IX	2984 2954	33510 33850	3300
X	2812 2793	35560 35800	3900	X	2907 2890	34400 34600	3250

TABLE IVB.—Solution Spectra of β-Naphthol.

Band	*In Hexane* λ	1/λ	ε	*In Ethyl-Alcohol.* λ	1/λ	ε
			Part I.			
A	3304	30270	1570			
B	3277	30520	2090	3320	30120	1850
C	3237	30890	1570			
D	3205	31200	1510			
E	3135	31900	1820	3175	31500	1700
G	3091	32350	1450			
H	3065	32630	1510	3086	32400	1000
I	3003	33300	1050	3030	33000	725
			Part II.			
K	2861 2813	34950 35550	4070	2876 2856	34790 35010	3100
L	2756 2707	36290 36940	4900	2757 2728	36270 36660	4000
M	2645 2611	37810 38300	3900	2661 2621	37580 38150	3550
N	2546 2511	39280 39820	2320	2550 2518	39220 39710	2250

The total spectrum of α-naphthol differs from that of β-naphthol in that the two parts of the spectrum flow into one in the former and are clearly differentiated in the latter

The solution spectra of the naphthols in ethyl alcohol are shown in fig. 4. The average intensity has not noticeably altered Klingstedt* found that the 3 phenol bands in hexane became one in alcohol the whole curve being shifted 450 cm.$^{-1}$ towards the red. In Part II all the hexane bands are present, but their intensity has decreased by ε 1000. We find a similar reduction of ε 800 in the alcoholic phenol solution There is a possibility of tautomerism in the case of both phenol and the naphthols The following table gives the shift of the spectrum towards the red in cm.$^{-1}$ in relation to the vapour spectra.

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* 'C.R.,' vol. 174, p. 812 (1922).

	Phenol.	α-Naphthol		β-Naphthol	
		Part I	Part II	Part I	Part II
Vapour	0	0	0	0	0
In Hexane	290	350	800	350	800
In Ethyl Alcohol	700	600	1800	800	1100

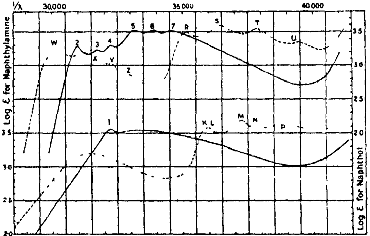

FIG 4.—Upper Curves : α-Naphthol (——) and β-Naphthol (- - - -) in Ethyl Alcohol. Lower Curves α-Naphthylamine (——) and β-Naphthylamine (- - - -) in Water

Both naphthalene and benzene show but very small variations in their absorption spectra when dissolved in alcohol or hexane, the same bands appearing in both solvents Alcohol is a strong dipole the electric fields of whose molecules must act with a sort of "Stark effect" on the dipoles of phenol and the naphthols Naphthalene and benzene on the other hand are electrically neutral, hence their absorption spectra are but little affected by dipolar solvents

Vapour spectra of the naphthols (see Table V and fig 3) The following frequency intervals occur for α-naphthol —

I_B (31459)–I_A (31082) = Δ'/λ 377 cm $^{-1}$
II (31880)–I_A (31123) = „ 757
IV (32640)–II (31880) = „ 760
V (32895)–III (32140) = „ 755

$$\frac{2272}{3} = 757 \text{ cm}^{-1}.$$

The interval 757 cm $^{-1}$ is almost certainly double the correct interval of 378 cm.$^{-1}$ which is probably caused by the atomic vibrations in the naphthol

TABLE V —Vapour Spectra of

α-Naphthol and *β-Naphthol*

Band.	λ	1/λ	
	Part I at 100° C		
I_A	3217,63	31078,8	
	3217,30	31082,0	
	3213,04	31123,2	
	3212,13	31132,0	
	3211,85	31134,7	
	3210,94	31143,5	
	3208,33	31168,9	
	3207,92	31172,8	
	3207,68	31175,2	
I_B	3182,52	31421,6	
	3180,64	31440,2	
	3180,44	31443,2	
	3180,26	31444,0	strong
	3180,04	31446,1	
	3179,62	31450,3	
	3179,48	31451,7	
	3179,29	31453,6	
	3179,13	31455,1	
	3178,92	31457,2	
	3178,70	31459,4	strong
II	3137	31880	edge
III	3111	32140	,,
IV	3064	32640	,,
V	3040	32895	,,
VI	2989	33510	maximum
VII	2943	33980	,,
	Part II at 75° C		
VIII	2912	34340	
	2890	34600	
IX	2851	35080	
	2819	35470	
X	2753	36320	
	2738	36520	

Band	λ	1/λ	
	Part I at 115° C		
A	3282	30470	edge
	3277	30520	,,
	3270,71	30574,4	,,
	3269,15	30589,1	,,
B	3238,19	30881,5	
	3236,60	30896,6	
	3236,18	30900,6	
	3235,94	30902,9	
	3235,39	30908,2	
	3230	30960	edge
C	3212	31130	,,
	3196	31290	,,
D	3168	31570	,,
	3159	31660	,,
E	3119	32060	
	3102	32240	,,
G	3071	32560	maximum
H	3042	32870	limits.
	3034	32960	
I	2980	33560	,,
	2965	33730	
	Part II at 90° C		
K	2823	35420	
	2785	35910	
L	2703	37000	
	2649	37750	
M	2601	38450	
	2557	39110	
N	2494	40100	
	2475	40400	

molecule In β-naphthol we find a similar interval of 382 cm $^{-1}$. Both the above periodicities represent that of 474 cm.$^{-1}$ which we find for naphthalene* vapour This indicates that the particular atomic configuration which gives rise to this interval has a greater mass in the naphthols than in naphthalene

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* 'Roy Soc Proc,' A, vol. 105, p. 662.

The strong bands B and I show a definite fine structure, which however even in Bands I_A and I_B are not sufficiently resolved to allow of an accurate determination of the moment of inertia The lines seem to be more closely spaced than in the case of naphthalene which indicates a greater moment of inertia for the former

Stang* has measured the *infra red* absorption spectra of the naphthols in CS_2 and CCl_4 The infra-red bands may be represented by the following formulæ where n and p are small whole numbers For α naphthol n (378) + p (110) and β naphthol n (382) + p (125) From Table VI we see that the observed and calculated values agree well together The constants 378 and 382 are those that appear in the U V absorption spectra In the case of α-naphthol we find three pairs of bands in Stang's measurements with an average frequency interval of 21 cm^{-1} 1626–1603 = 23, 1276–1255 = 21, 1048–1028 = 20 From this we can calculate the moment of inertia J Δ'/λ c — 6,3 10^{11} where c is the velocity of light *in vacuo* Hence

$$J = \frac{1{,}37 \quad 10^{-16} \quad 300}{(6{,}3 \quad 10^{11})^2} = \frac{4{,}11 \quad 10^{-14}}{4{,}335 \quad 10^{24}} = 94{,}8 \quad 10^{-40}\, g\, \text{cm}^2$$

We can find *only one* such pair in the case of β-naphthol, namely, 1028–1010 = Δ^k/λ 18 cm^{-1} which gives a J value of 142,5 10^{-40} g cm^2 Hence β has a greater J than α which would appear to be theoretically correct The cathodoluminescence of both naphthols have been examined by Fischer† who found that each spectrum consisted of two parts, the bands of the first half being sharp and those at the blue end being broad and continuous Dickson‡ has measured a few fluorescence bands. The production of these various forms of emission are explainable on the same grounds as for naphthalene §

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* 'Phys. Rev,' vol. 9, p 544 (1917)

† 'Z f. Wiss Phot,' vol. 6, p 315 (1906).

‡ 'Z. f Wiss. Phot,' vol 10, p 166 (1911)

§ H. de Laszlo, 'Z f. Phys Chem.,' vol. 118, p 395 (1925)

TABLE VII—continued—Solution Spectra of

α-Naphthonitrile and β-Naphthonitrile in Hexane

Band	λ	1/λ	ε	Band	λ	1/λ	ε
	Part II				Part II		
V	3042	32870	3980	H	2939	34030	3150
	3015	33170			2912	34340	
VI	2975	33610	5300	I	2891	34590	3150
	2890	34600			2866	34890	
VII	2845	35150	4680	K	2831	35320	4570
	2786	35880			2798	35740	
				L	2778	36000	4400
					2752	36340	
				M	2716	36820	4400
					2692	37150	
				N	2675	37380	4100
					2656	37650	
				O	2628	38050	3800
					2614	38260	

The vapour spectra of the naphthonitriles show no new bands (Table VIII). Fischer* finds two sets of bands for β-Naphthonitrile in the spectrum of its cathodoluminescence, that at the red end being narrow and the set in the blue portion being broad and diffuse This phenomenon is again the same as in naphthalene

The *Naphthoic acids* (see fig 6 and Table IX) α-crystallised well from 80 per cent alcohol and melted at 160° C, while β melted at 184° C The solution spectra in hexane show very steep absorption limits which are shifted 1950 cm $^{-1}$ for α and 2750 cm $^{-1}$ for β towards the red in comparison with naphthalene Klingsted and Castille† find a similar shift of 3050 cm $^{-1}$ for benzoic acid in relation to benzene, all but three of the latter's bands were fused into one, and the intensity (ε) of the curve was doubled The —COOH group has the same

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* 'Z f. Wiss Phot.,' p. 315 (1908).

† 'C R,' vol. 176, p. 749 (1924).

TABLE VIII

Vapour Spectra of {α Naphthonitrile Part I at 120° C Part II at 60° C
{β Naphthonitrile Part I at 125° C Part II at 60° C

α Naphthonitrile

Band	λ	1 λ
	Part I	
I	3219 3175	31070 31500
II	3164 3154	31610 31710
III	3107 3090	32190 32270
IV	3075 3047	325.0 328 0
	Part II	
V_I	2980 2955	33560 33840
V_{II}	2935 2920	34070 34240
VI	2882 2797	34700 35760
VII	2765 2717	36160 36800

β Naphthonitrile

Band	λ	1/λ
	Part I	
A	3280 3244	30490 30830
B	3200 3155	31250 31700
C	3146	31790
D	3127 3095	31980 32310
E	3065 3031	32630 32990
G	2987 2960	33480 33780
	Part II	
H	2849 2840	35100 35210
I_1	2813 2807	35550 35630
I_2	2788 2781	35870 35960
K	2756 2740	36290 36500
L_1	2716 2706	36820 36950
L_2	2687 2669	37220 374 0
M	2651 2638	37720 37910
N	2617 2610	38210 38310
O	2590 2572	38610 38880

effect on the naphthalene curve It seems as though in the case of the naphthoic acids and α-Naphthylamine molecules only one degree of activation takes place instead of two as with the $-CH_3$, Br, Cl, OH, and $-$ CN derivatives.

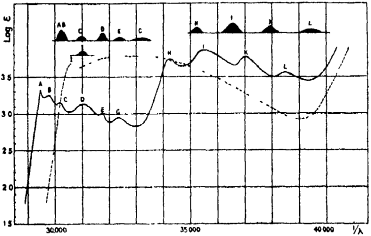

FIG 6 —Naphthoic Acid in Hexane

α-Naphthoic Acid I, $t = 165°$
β-Naphthoic Acid A-G, $t = 180°$; H-L, $t = 145°$

TABLE IX

α-Naphthoic acid

Solution Spectrum in Hexane				Vapour Spectrum		
Band	λ	1/λ	ε	Band.	λ	1/λ
Part I				Part I at $t = 165°$ C.		
I	3280	30490	5000	I	3237	30890
	3250	30780			3213	31120
Part II				Part II		
Consists of a very wide flat band whose approximate limits are :—				Consists likewise of a very broad fla band with very indefinite limits.		
	3175	31500	6000			
	2900	34500				

TABLE IX—continued

β-Naphthoic acid

Solution Spectrum in Hexane				Vapour Spectrum		
Part I				Part I at t = 180° C		
A	3398 3388	29430 29515	2150	AB	3326 3288	30070 30410
B	3360 3350	29760 29850	1850	C	3247 3222	30800 31040
C	3324 3296	30080 30340	1450	D	3162 3143	31630 31820
D	3278 3195	30510 31300	1300	E	3102 3070	32240 32570
E	3162 3141	31630 31840	1150	G	3033 2987	32970 33480
G	3115 3058	32100 32700	890			
Part II				Part II at t = 145° C		
H	2937 2911	34050 34340	5500	H	2853 2830	35050 35340
I	2836 2770	35260 36100	7250	I	2756 2719	36290 36780
K	2716 2675	36820 37380	5900	K	2654 2621	37680 38150
L	2607 2573	38360 38860	3600	L	2555 2515	39140 39760

The α-acid shows no structure while the β-body has a number of weak bands which form definite series. D (30900)-A (29470) = 1530 cm $^{-1}$, E (31740)-C (30210) = 1530 cm $^{-1}$, G (32400)-D (30900) = 1500 cm $^{-1}$, which gives 1520 cm $^{-1}$ as an average value.

The *Naphthylamines.*—Melting point of α 50° C. and of β 111° C.

Solution spectra in hexane (see Table X and fig. 7). The $-NH_2$ group has a similar influence on naphthalene as it has on the benzene spectrum. Thus Klingstedt* finds that the absorption limit of benzene is shifted 4660 cm $^{-1}$ to the red, while we get similar shifts of 3500 cm. $^{-1}$ and 4050 cm $^{-1}$ for the α and

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* 'C.R.,' vol. 176, p. 248 (1924).

TABLE X —Solution Spectra of

α-Naphthylamine in Hexane.				*α-Naphthylamine in Water*			
Band	λ	1/λ	ε	**Band**	λ	1/λ	ε
	Part I				Part I		
I	3350	29850	4900	I	3284	30450	3650
	3310	30210			3238	30880	
	Part II				Part II		
Very shallow broad band with approximate limits —				Same width as in hexane, but rather flatter			
V	3226	31000	5150	V	ε = 3550		
	2985	33500					

β-Naphthylamine in Hexane				*β-Naphthylamine in Water*			
Band	λ	1/λ	ε	**Band**	λ	1/λ	ε
	Part I				Part I		
A	3550	28170	740				
B	3500	28570	1550		A strong broad band		
D	3445	29030	1700	**A–H**	3448	29000	1550
G	3390	29500	1850		3226	31000	
H	3335	29985	2000				
	Part II				Part II		
K	2913	34330	4600	**K + L**	2914	34320	3800
L	2875	34780	3900		2885	34660	
M	2813	35550	6000	**M**	2812	35560	4900
	2791	35830			2777	36010	
N	2771	36090	5000	**N**	2768	36130	4300
	2758	36260			2756	36290	
P	2708	36930	5650	**P**	2693	37120	4900
	2656	3765			2659	37610	

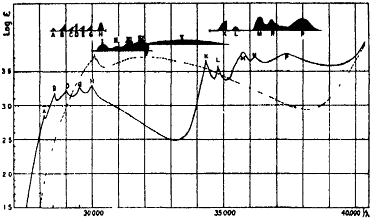

FIG 7 —Naphthylamine in Hexane

α-Naphthylamine A-H, $t = 110^\circ$, K-P, $t = 95^\circ$
β Naphthylamine I IV, $t = 95^\circ$, V, $t = 90^\circ$

β-positions on introducing a $-NH_2$ group into naphthalene In β-napthylamine we find the following periodicities —B–D = 460 cm^{-1}, D–G = 470 cm^{-1}, G-H 485 cm^{-1}, of which 472 cm^{-1} is an average Aniline has ten narrow bands whose interval is 450 cm^{-1} with an ϵ value 6 × greater than benzene

For solution spectra in water (see fig 5 and Table X) Band I appears at the following frequencies when measured in various physical states which result will be discussed in a later paper in hexane 30030, in water 30680, in alcohol 30350, in vapour 30410 cm

The vapour spectra (see fig 7 and Table XI) of α give an interval of 500 cm^{-1} which is greater than that of naphthalene (474,4 cm^{-1}), III (31410)-II (30910) = 500 cm^{-1}, II (30910)-I (30410) = 500 cm^{-1}

TABLE XI —Vapour Spectra of *α-Naphthylamine* and *β-Naphthylamine*

α-Naphthylamine

Band	λ	1/λ
	Part I at 90° C	
I	3306 3271	30250 30580
II	3246 3224	30810 31020
III	3200 3168	31250 31570
IV	3158 3129	31670 31960
	Part II at 90° C Consists of a broad flat band	
V	3095 2848	32310 35110

β-Naphthylamine

Band	λ	1/λ	
	Part I at 130° C		
A	3515 3500	28450 28570	
B	3466,34 3464,71 3463,18 3462,74 3461,55 3458,55 3455 92 3433,99	28849,9 28862,4 28875,2 28878,9 28888,8 28913,9 28935,9 28952,0	
C	3428,28 3427,45 3426,69 3425,26 3424,50 3423,90 3421,19 3420,83 3420,44 3418,75 3418,23	291,691 29176,2 29182,7 29194,9 29201,3 29206,5 29229,6 29232,7 29236,0 29250,5 29254,9	 strong strong
D	3404,3 3402,4 3400,8 3398,6 3397,2	29375 29391 29405 29424 29436	
E	3378,6 3377,0 3375,2 3373,6 3367,6	29598 29612 29628 29642 29695	
G	3342,4 3339,6 3336,8 3322,5	29919 29944 29969 30098	
H	3304 3289	30240 30400	

β-Naphthylamine

Band	λ	1/λ
	Part II at 95° C	
K	2871 2848	34830 35110
L	2829 2814	35350 35540
M	2762 2739	36210 36510
N	2723 2708	36720 36930
P	2661 2611	37580 38300

The following frequency intervals appear in β-naphthylamine vapour :—

G (30098)–E (29695) = 403
E (29642)–C (29250) = 392
C (29250)–B (28862) = 388
E (29598)C–C (29206) = 392
E (29628)–C (29236) = 392

Average 392 cm $^{-1}$

D (29408)–C (29169) = 239
E (29642)–D (29408) = 234
C (29169)–B (28936) = 233

Average 235 cm. $^{-1}$

The interval 392 probably corresponds to the big period of naphthalene vapour Hence we conclude that those atomic groupings which give rise to these periodicities are heavier in β-naphthylamine than in naphthalene Fischer[*] has photographed the cathodoluminescence, and Stark and Steubing[†] have measured the fluorescence Stang[‡] found the following infra-red absorption bands for β-naphthylamine in CS_2 and CCl_4 most of which can be expressed by the formula $n392 + p235$ where n and p are small whole numbers and the two constants frequency intervals which appear in the U V vapour spectrum (See Table XII) We find only one double edge in Stang's results 1188-1164 = 24 cm $^{-1}$ This gives a J value of $80{,}4 \times 10^{-40}\, g$ cm ^{2} For α naphthylamine there are two sets of double edges, 1406–1376 = 30 cm $^{-1}$, 1124-1098 = 26 cm $^{-1}$, average 28 cm $^{-1}$, which gives a moment of inertia $59{,}0 \times 10^{-40}\, g$ cm $^{-2}$

TABLE XII

− n	9	8	2	2	3	5	2
p	0	0	7	6	2	0	3
1/λ calc	3516	3124	2429	2194	1646	1960	1489
μ calc.	2,84	3,20	4,12	4,55	6,08	5,10	6,71
μ obs.	2,86	3,25	4,12	4,44	6,13	5,22	6,66
1/λ obs.	3406	3078	2427	2252	1631	1915	1502
	3		2	3		2	
	1		2	0		1	
Calc	1411	—	1254	1176		1019	
Calc	7,10	—	7,99	8,51		9,81	
Obs	7,20		8,09	8,41 8,59		9,76	
Obs.	1389	1294	1236	1188	1134	1025	
				1164			

Some other Physical Properties of the Naphthalene Series

Auwers and Krollpfeiffer[§] have measured the exaltation of refractivity for a number of monoderivatives, and find that this value is invariably greater for the β than for the α-isomer Both the boiling and melting points of the β-compounds are higher than their isomers

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[*] 'Z f Wiss Phot,' vol. 6, p 315 (1908)

[†] 'Phys Z,' vol 9, p 481 (1908).

[‡] 'Phys Rev,' vol. 9, p 544 (1917)

[§] 'Ann. d. Chem.,' vol. 335, p. 230.

Influence of Chemical Constitution on the Absorption Spectra of the Naphthalene Series

The absorption spectra of the β-derivatives are more like that of naphthalene than their isomers and contain a larger number of bands Since naphthalene is a fairly rigid molecule as shown by its fine structure* we can assume that the groups are held more firmly in the β than in the α-positions α-Naphthol and α-naphthylamine are more easily oxidised than their isomers Naphthalene forms addition products with greater facility than benzene, and is likewise more readily oxidised The former will therefore be the least saturated of the two bodies This is borne out by the fact that its absorption (ε) is about ten times that of benzene and the whole has been shifted to the red

The halogen compound of naphthalene are chemically unreactive and their spectra differ but little from that of the parent body The halogens seem to act rather through their weight than by means of electrostatic forces with which they might upset the equilibrium of the molecule One would expect, therefore, that a sufficient number of halogen atoms on the molecule would cause the latter to cease rotating, leaving only the broad shallow band due to electron jumps This indeed we find to be the case with octo-chloronaphthalene

Chemically the naphthols are similar to the phenols, tautomerism being possible in both cases with the formation of an addition product with alcohol or water. The nitriles which are very labile contain an unsaturated trivalent N which is very active in increasing and forming very many well-marked bands without causing any great shift towards the red The NH_2 group contains a saturated trivalent N, hence a reduction in the number of bands The nitronaphthalenes possess no structure at all This property of removing band structure seems to be characteristic of pentavalent N and especially for the NO_2 group The $-COOH$ group likewise wipes out all structure and shifts the absorption far into the red though not so far as the NO_2 group This may be due to the two oxygen atoms being bound to a common atom.

We have recently been examining cis- and trans-dekalin. Both are transparent to U V as cyclohexane This is what one would expect when all the double bonds have vanished Tetralin has a characteristic absorption whose bands lie between ε 150 and ε 300 (λ 2500- λ 3000). In other words it behaves spectroscopically like a benzene derivative with an aliphatic side chain which agrees well with its chemical properties

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* 'Roy Soc Proc.,' A, vol. 105, p. 578 (1924)

Summary

(*a*) Those derivatives of naphthalene containing the groups CH_3 Cl Br, OH, COOH, CN and NH_2 show a marked difference in absorption spectra depending on whether the groups are in the alpha or beta positions

(*b*) The spectra of the beta-derivatives are more like that of naphthalene than their isomers

(*c*) The beta spectra consist of two clearly differentiated sections both as regards position and intensity (ε) The first part is always more shifted towards the red than the second part when compared with naphthalene

(*d*) In the alpha spectra things are reversed Part II having a greater shift towards the red than Part I β Naphthol has its Part II shifted towards the ultra violet which is quite anomalous Table XIII shows the red shift for the various derivatives examined when compared with the parent substance

TABLE XIII

	Part I	Part II
	cm^{-1}	cm^{-1}
α CH_3	330	1000
β CH_3	620	100
α Br	720	1200
β Br	800	500
α Cl	670	1110
β Cl	730	395
α COOH	1950	—
β COOH	2750	750
α OH	1200	—
β OH	2100	400
α NH_2	3500	4000
β NH_2	4050	500
α CN	1250	2500
β CN	1750	650

TABLE XIV

	Part I	Part II
Benzene	280	
Naphthalene	260	505
α CH_3	90	900
β CH_3	150	800
α NH_2	300	—
β NH_2	350	625
α OH	350	800
β OH	350	800
α CN	120	1050
β CN	290	800
α COOH	350	—
β COOH	650	950
α Br	200	850
β Br	200	850

(*e*) The amount of the red shift is of the same order in the case of naphthalene and benzene derivatives except that it is always a little bigger in the latter case

(*f*) Part I of the beta spectra always consists better defined intenser and more numerous bands than the alpha spectra They also contain one very prominent band which corresponds with band C of naphthalene and in the case of vapour often possesses a fine structure

(*g*) The hexane solution spectra are always shifted towards the red when compared with the vapour spectra Perhaps this is due to the fact that every molecule possesses a different electrical moment When in solution the molecule finds itself in a strong electric field due to the molecules of solvent which acts with a sort of Stark effect on the absorption bands of the dissolved molecules The amount of this effect will of course vary with the electric moment hence the red shift will be different for every body

(*h*) The red shift (*g*) is greater for Part II than Part I This likewise indicates a Stark effect for the action of an electric field is stronger the higher the electronic energy level is in the molecule Since Part II represents a higher state of electronic activation than Part I we would therefore expect the above result The amount of this red shift for various bodies is shown in Table XIV

(*i*) The average intensity (ε) of the beta spectra (Part I) increases in the order of the following groups Br Cl CH_3, CN COOH OH and NH_2 Part II of all derivatives except for the naphthylamines have the same ε as for naphthalene

(*k*) The following derivatives possess a fine structure in the state of vapour β-CH_3, and $\alpha + \beta$-OH β NH_2 β Br and β-Cl The following only have a sharp band edge for one band representing band C of naphthalene α-Br and $\alpha + \beta$-CN and α-CH_3

TABLE XV

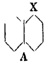
	Solution	Δ/λ cm^{-1}	Vapour	Δ/λ	cm^{-1}
Naphthalene	1450	450	474 4	+203,4	+ 62 7
α CH_3	1540		413		
β CH_3	1425	328			
α Br	1480	540			
β Br	1470	506			
α OH	1470		378		
β OH	1420		382		
β COOH	1520				
α CN	1450	480			
β CN	1460				
α NH_2			(500)		
β NH_2		470	392	235	

(*l*) The bands of most of the bodies examined can be ordered into simple series These periodicities which represent the oscillation frequencies of the atoms in the molecule may be seen in Table XV From this we see that the vapour periods are always smaller than that of naphthalene which is to be expected if an atomic grouping is weighted down by the addition of a new group however small The vapour periods appear again in the infra red spectra

(*m*) The moments of inertia calculated from the infra red absorption bands are as follows —

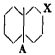
α Naphthol 94 8 10 ^{40} g cm ^{2}

α Naphthylamine 59 0 10 ^{40} g cm ^{2}



β Naphthol 142 5 10 ^{40} g cm ^{2}

β Naphthylamine 80 4 10 ^{40} g cm ^{2}



Hence we see that I is less for the alpha than for the beta body This seems probable if the molecule rotates round the axis A for then the group X is nearer the axis in the alpha than in the beta position

A Comparison between Unimolecular and Bimolecular Gaseous Reactions. The Thermal Decomposition of Gaseous Acetaldehyde.

By C. N. HINSHELWOOD, Fellow of Trinity College, Oxford, and
W. K. HUTCHISON, Scholar of Corpus Christi College

(Communicated by Dr. N. V. Sidgwick, F.R.S.—Received March 23, 1926.)

We have recently observed that the thermal decomposition of acetone in the gaseous state is a homogeneous, unimolecular reaction. As in the decomposition of nitrogen pentoxide, the number of molecules which react in unit time is very many times greater than the number which could receive the necessary energy by collision with other molecules. With the object of seeing whether this fundamental characteristic of unimolecular reactions would be confirmed in yet another instance, we have examined the thermal decomposition of gaseous acetaldehyde, which at 500° C. decomposes smoothly into methane and carbon monoxide. The chemical similarity between this and the decomposition of acetone made it seem probable that acetaldehyde might also decompose in a unimolecular manner. But although the new reaction proved to be homogeneous, it was bimolecular.

We therefore have the opportunity of making a comparison between the molecular statistics of two chemically similar reactions taking place in the same region of temperature, one of which definitely depends on molecular collisions, while the other appears to be independent of them. The contrast between the two supports strongly our previous theoretical conclusions, because, while in the unimolecular reaction the number of molecules reacting bears no relation whatever to the number which could be activated by collision, in the bimolecular reaction there is almost perfect correlation between the number of collisions suffered by activated molecules and the observed rate of reaction.

The aldehyde appears to decompose smoothly according to the equation

$$CH_3CHO \rightarrow CH_4 + CO$$

The observed increase of pressure amounted to 98 per cent. of the theoretical value. The decomposition products contained no carbon dioxide or unsaturated hydrocarbons. Three analyses gave the following percentages of carbon monoxide:—

50·7, 51·3, 50·5.

The residual gas after removal of carbon monoxide was analysed in a Haldane apparatus with the following result

0.632 c.c. gave on combustion a contraction of 1.292 c.c. and 0.645 c.c. of carbon dioxide

This corresponds almost exactly to methane but a mixture of one volume of hydrogen with one volume of ethane would give exactly the same analysis as two volumes of methane. Since the reaction is kinetically bimolecular it is possible that it might take place in accordance with the equation

$$2CH_3CHO \rightarrow C_2H_6 + H_2 + 2CO$$

rather than with the equation

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO$$

But the actual products were shown to consist of methane and not a mixture of ethane and hydrogen by comparing their thermal conductivity with that of an artificially prepared mixture.

The apparatus and experimental method were exactly as in the experiments on the decomposition of acetone. The purest obtainable acetaldehyde was dried and redistilled before use. The actual method of manipulation whereby quite rapid rates of reaction can be measured accurately has already been described.*

The course of the reaction is bimolecular as the following typical experiment shows

Temperature 518° C

Initial pressure = 363 mms (a)

Time in seconds t	Pressure change in mms x	$k = \frac{1}{t}\left\{\frac{1}{a-x} - \frac{1}{a}\right\}$
42	34	6.79×10^{-6}
73	54	6.69
105	74	6.71
190	114	6.64
242	134	6.66
310	154	6.55
384	174	6.61
480	194	6.59
665	224	6.68
840	244	6.72
1 070	264	6.86
1 440	284	6.88
		Average 6.69×10^{-6}

The corresponding value of k with a and x expressed in gram molecules per litre is 0.331

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* J. Chem. Soc. vol. 125 p. 393 (1924)

The experiments were carried out in a bulb with a fine capillary neck and connections so that the dead space was quite negligibly small When the reaction is complete the pressure should have increased to exactly twice its initial value The observed increase was 98 per cent We are therefore justified in using x the pressure increase together with a the initial pressure without change of units

The constancy of the numbers in the last column, although satisfactory is not conclusive The best test of a bimolecular reaction is variation of the initial pressure The time taken for a given fraction of the reaction to complete itself should be inversely proportional to this In the following table are given a number of results obtained at 518° C

Initial pressure	Time required for half the change τ	Time required for three-quarters of the change τ'	Ratio τ'/τ
479	328	—	—
420	385	1 135	2 95
363	420	1 210	2 9
290	492	1 400	2 85
225	5 2	1 710	3 0
184	665	1 920	2 9
121	820		—
60	1 400	—	—
337	440	(In this experiment 250 mms of reaction products from a previous experiment were present initially)	
232	560	(312 mms products present initially)	

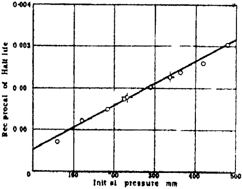

Fig —Curve showing Bimolecular Nature of the Decomposition of Acetaldehyde at 518° C The two points marked by a cross ⚲ correspond to experiments in which the products of reaction were present initially

The figure shows that the relationship between the initial pressure and the reciprocal of the half life is accurately linear It is to be noted however that the line does not pass through the origin Incidentally it will be observed that the products of reaction are without effect on the rate Another convenient test of a bimolecular reaction is the relation between the times required for one half and three quarters respectively of the total change to take place They should be exactly as 1 3 The examples given in the last column of the above table show that this test also is satisfied

The reaction is almost completely homogeneous It went at the same rate in two different bulbs

Temperature 518° C

	Initial pressure	k	Mean
Bulb I	363 290	0 333 0 359	0 342
Bulb II	360 306	0 350 0 349	0 350

The addition to the reaction bulb of a large quantity of powdered silica which should have increased the surface area some twenty times caused an increase in the rate of reaction of 30 per cent only

Initial pressure	k	
364	0 461	0 469
319	0 477	

At a lower temperature 464° C the values were

$k = 0\ 049$ in the empty bulb and

$k = 0\ 066$ in the bulb with silica powder

The reaction as it takes place in the empty bulb cannot therefore be heterogeneous to the extent of more than a very small fraction at these pressures At quite low pressures the disturbance might possibly become serious This may account for the failure of the line in the figure to pass through the origin

The following table gives the values of k found at different temperatures f r the homogeneous reaction

k is expressed throughout with the time in seconds and the concentration in gram molecules per litre

T (abs)	k_{observed}	$k_{\text{calculated}}$
865	4 76 5 13 } av 4 95	4 70
836	2 19 2 08 } 2 14	1 82
811	0 755 0 826 } 0 79	0 78
791	0 352 0 333 } 0 343	0 38
759	0 104 0 106 } 0 105	0 107
733	0 0361 0 0343 } 0 0352	0 036
703	0 0103 0 0117 } 0 0110	0 0096

The heat of activation calculated from these results is 45,500 calories for two gram-molecules The velocity constant of a bimolecular reaction is of the form

$$k = \mathrm{C}\sqrt{\mathrm{T}}e^{-\mathrm{E}/\mathrm{RT}}$$

Evaluating the constant, we find that the results can be summarised in the equation

$$\mathbf{k} = 5\ 5 \times 10^{10}\ \sqrt{\mathbf{T}}\ e^{-45\ 500/\mathrm{RT}}$$

The calculated values of the constants, given in the last column, were obtained from this equation The agreement is seen to be very close

The rates of other bimolecular reactions can be calculated from the equation

(*Number of molecules reacting*)

= (*Number of molecules entering into collision*) $\times\, e^{-\mathrm{E}/\mathrm{RT}}$

The present instance should be a particularly crucial test, since, as we have already seen, in the chemically similar unimolecular decomposition of acetone, the number of molecules reacting is about 10^5 times greater than the number which collide possessing the requisite energy of activation

For the decomposition of acetaldehyde at 800° Abs the value of the velocity constant is 0 520 From this we find, taking Avogadro's Number as $6\ 06 \times 10^{23}$ that the number of molecules reacting per second in one c c. at 760 mm. is

$$7\ 3 \times 10^{16}$$

Taking the diameter of the aldehyde molecule as 5×10^{-8} cm. we find that the number of collisions calculated from the formula $\sqrt{2}\pi\sigma^2\bar{u}n^2$ is $6\ 38 \times 10^{28}$.

At this temperature the fraction $e^{-E/RT}$ has the value $3·4 \times 10^{-13}$ whence we find that the number of molecules which might be expected to react is

$$4·3 \times 10^{16}$$

This agrees within a factor or two with the number actually observed to react. The contrast between this agreement and the discrepancy of 10^5 found in the unimolecular reaction, confirms the conclusion that the method of activation in unimolecular reactions is fundamentally different from any which involves molecular collisions.

It may be remarked that this reaction provides one more instance, if one were needed, of the rule that the region of temperature in which a bimolecular reaction attains a given rate, is determined by the magnitude of its heat of activation, and that other specific factors can play but a minor part in determining the rate of reaction.

Summary

The thermal decomposition of acetaldehyde in the gaseous state has been investigated over the temperature range 430° – 592° C.

The reaction is bimolecular, and under the conditions of the experiments practically entirely homogeneous.

The rate of reaction can be calculated from the equation

$$k = 5·5 \times 10^{10}\sqrt{T}\ e^{-45,500/RT},$$

k being expressed in gram-molecules per litre per second.

On the assumption that pairs of molecules react, which on collision have a minimum joint energy of 45,500 calories (for two gram-molecules), the rate of reaction can be calculated from kinetic considerations, and is shown to be in close agreement with experiment.

The contrast between this reaction and the chemically very similar decomposition of acetone is illuminating. The latter reaction, being unimolecular, is not necessarily dependent on collisions, and it is indeed found that the number of molecules transformed in unit time is 10^5 times greater than the number which could receive the heat of activation from collisions. In the bimolecular decomposition, on the other hand, there is almost the exact relation between heat of activation, number of collisions, and rate of reaction, which the simplest theory predicts.

A General Configuration in Space of any Number of Dimensions Analogous to the Double-Six of Lines in Ordinary Space

By T G Room, B.A

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The double-six of lines in ordinary space had attention first drawn to it by Schläfli[*] in his discussion of the arrangement of the lines on the cubic surface Some time later, Bordiga[†] in a paper on the projectively generated sextic surface[||] in [4], pointed out the existence of a similar double configuration of ten lines and ten planes in [4], the lines lying on the surface and the planes cutting it in cubic curves Further work on this surface has[‡] more recently been done by White In a later paper still,[§] White considered the generalization of these two surfaces, namely, the projectively generated surface of order $\frac{1}{2}n(n-1)$ in $[n]$, and showed that, as stated by Bordiga, there are on it $\frac{1}{2}n(n+1)$ lines Although not mentioned in that paper, it is clear from the work there that there are $\frac{1}{2}n(n+1)$ $[n-2]$s, each of which cuts the surface in a curve of order $\frac{1}{2}(n-1)(n-2)$, and meets all but one of the lines. These $[n-2]$s and lines, therefore, form a double-$\frac{1}{2}n(n+1)$ in $[n]$

In this paper the existence of a double configuration of greater generality than this is indicated It is shown that if p, q and r are any positive integers with $r < p$ and q then —

> *In space of $r(p+q-r)-2$ dimensions it is possible to find a family of* N *spaces of dimension $r(p-r)-1$, and a family of* N *spaces of dimension $r(q-r)-1$ such that each space of either family meets all but one of the spaces of the other*

$$\mathrm{N} = \frac{(p+q-2r)!\,(p+q-2r+1)!\,\ldots(p+q-r-1)!\;1!\,2!\,\ldots(r-1)!}{(p-r)!\,(p-r+1)!\ldots(p-1)!\,(q-r)!\,(q-r+1)!\ldots(q-1)!}.$$

Such a configuration will be called a double-N, and n will frequently be written for $r(p+q-r)-2$, the dimension of the space in which it lies.

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[*] 'Quart Journ.,' vol. 2, pp 55 and 110 (1858).

[†] 'Atti R. Acad. Linc. (Mem.), vols. 4, 4A, p. 182 (1887).

[‡] 'Camb. Phil Soc Proc.,' vol. 21, p. 216 (1922).

[§] *Ibid*, vol. 22, p. 1 (1924)

[||] A (planar) space of n dimensions is denoted by $[n]$.

The special cases cited above are those of—

$p = q = n = 3$, $r = 1$ the double-six
$p = 3$, $q = n = 4$, $r = 1$ the double-ten
$p = 3$, $q = n$, $r = 1$ the double-$\frac{1}{2}n(n+1)$

A $[r(p-r)-1]$ in $[r(p+q-r)-2]$ is represented by $qr-1$ independent linear equations in the co-ordinates of the $[r(p+q-r)-2]$. To obtain the double-N configuration, qr equations of a certain form are taken, connecting whose terms is one identical linear relation. The equations contain pr parameters, but in consequence of the existence of the linear identity, there is a number of relations connecting these, a number large enough, in fact, to make finite the number of spaces represented by the equations, when the parameters take all possible sets of values. Further, given a suitable set of parameters, the constants in the identical relation are uniquely determinable. Regrouping the terms of the original equations with these as parameters, instead of the former set, pr linear equations are obtained, which are connected by one linear identity, and represent therefore a $[r(q-r)-1]$. Thus each of the $[r(p-r)-1]$s is associated with a unique $[r(q-r)-1]$, and, from the form of the equations, *vice versa*. Also it can be shown that any $[r(p-r)-1]$ does not meet the $[r(q-r)-1]$ with which it is associated, but does meet all those associated with the other $[r(p-r)-1]$s. These two families of spaces form therefore a double-N.

This double configuration is not in general self-dual, as are the double-six of lines in [3], and the other special configurations mentioned at the beginning, but is so when $r = 1$. It is then the double-$\dfrac{(p+q-2)!}{(p-1)!\,(q-1)!}$ of $[p-2]$s and $[q-2]$s in $[p+q-3]$. It might be expected, in analogy with the double six of lines, that this self-dual configuration would have a quadric (Schur quadric*) w r to which it is self-polar. Except in the cases of the double-six, and the simplex in $[n] - p = 2$, $r = 1$, $q = n+1$, it is shown that there can be no such quadric. The process adopted in the proof of the existence of this simpler type of configuration is very similar to that indicated above for the general case, but the algebra is considerably shorter, moreover, some of the equations arising are required in showing that there is no Schur quadric, and it has therefore been thought advisable to give the proof of the theorem in its less complicated form first.

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* *Cf* Baker, 'Principles of Geometry,' vol. 3, pp. 162, 187, etc.

1 *In space of* $p + q - 3$ *dimensions it is possible to find a family of* N *spaces of dimension* $p - 2$, *and a family of* N *spaces of dimension* $q - 2$, *such that each space of either family meets all but one of the spaces of the other*

$$N = \frac{(p+q-2)!}{(p-1)!\,(q-1)!}$$

$$(n = p + q - 3, \quad r = 1).$$

Take as co-ordinates, in the $[n]$, $x_1, x_2, \dots x_\epsilon, \dots x_{\overline{n+1}}$, and let $x_{11}, x_{12}, \dots x_{\alpha\beta}, \dots x_{pq}$ be pq arbitrary linear functions of them of the form

$$x_{\alpha\beta} = a_{\alpha\beta 1}x_1 + a_{\alpha\beta 2}x_2 + \dots + a_{\alpha\beta\overline{n+1}}x_{\overline{n+1}}$$

the $a_{\alpha\beta\epsilon}$ being known constants. Adopting the convention of summation over like (Greek) suffixes, these equations will be written —

$$\left.\begin{array}{ll} x_{\alpha\beta} = a_{\alpha\beta\epsilon}x_\epsilon & \alpha = 1, \dots p \\ & \beta = 1, \dots q \\ & \epsilon = 1, \dots n+1 \end{array}\right\} \qquad 1.1$$

The same Greek letter will be used throughout as suffix to denote the same range of values.

Consider the q equations —

$$\left.\begin{array}{l} A_1x_{11} + A_2x_{21} + \dots + A_px_{p1} = 0 \\ A_1x_{12} + A_2x_{22} + \dots + A_px_{p2} = 0 \\ \quad \cdot \quad \cdot \\ A_1x_{1q} + A_2x_{2q} + \dots + A_px_{pq} = 0 \end{array}\right\}$$

or more shortly

$$A_\alpha x_{\alpha\beta} = 0, \qquad 1.2$$

in which the quantities are A_α arbitrary parameters. For these to represent a $[p-2]$, *i.e.*, a $[n-q+1]$, there must be one identical relation connecting the left-hand sides. Suppose this is—

$$B_1(A_\alpha x_{\alpha 1}) + B_2(A_\alpha x_{\alpha 2}) + \dots + B_q(A_\alpha x_{\alpha q}) = 0,$$

i.e.,

$$B_\beta A_\alpha x_{\alpha\beta} = 0. \qquad 1.3$$

This identity in the x_ϵ is equivalent to the $n + 1$ equations

$$B_\beta A_\alpha a_{\alpha\beta\epsilon} = 0. \qquad 1.4$$

By eliminating the B_β we obtain the conditions that must be satisfied by the A_α in order that the equations 1 2 may represent a $[p-2]$, namely

$$\left|\begin{array}{lll} A_\alpha a_{\alpha 11}, & A_\alpha a_{\alpha 12}, & A_\alpha a_{\alpha 1 n+1} \\ A_\alpha a_{\alpha 21}, & A_\alpha a_{\alpha 22}, & A_\alpha a_{\alpha 2 \overline{n+1}} \\ & & \cdot \\ A_\alpha a_{\alpha q 1}, & A_\alpha a_{\alpha q 2}, & A_\alpha a_{\alpha q n+1} \end{array}\right\| = 0 \qquad 1\ 5$$

The excess of the number of columns over the number of rows in this matrix is $p-2$, and the number of A_α is p, so that, save for a common multiple, a finite number of sets of A_α can be found which satisfy the matrix equation Among the whole family of $[p-3]$s represented by the equations

$$A_\alpha x_{\alpha\beta} = 0 \qquad 1\ 2$$

in which the A_α are arbitrary, there is, therefore, a finite number of $[p-2]$s

Any set of A_α which satisfies the equations 1 5 determines uniquely, save for a common factor, by means of equations 1 4, a set of B_β, *i e*, any $[p-2]$ given by the q equations

$$A_\alpha x_{\alpha\beta} = 0 \qquad 1\ 2$$

is associated with a unique $[q-2]$ given by the equations

$$B_\beta x_{\alpha\beta} = 0, \qquad 1\ 6$$

the left-hand sides of these equations being connected by the identical relation 1 3

It can now be shown that these two families of spaces have the required intersection property, namely, that any $[p-2]$ given by the equations 1 2, in which the A_α satisfy the matrix equation 1 5, meets all the $[q-2]$s of the other family, except that with which it itself is associated Take A^i_α to be the particular set of A_α, and B^j_β to be any set of B_β, except that obtained from the A^i_α by the equations 1 4 It has to be shown that the $[p-2]$

$$\left.\begin{array}{ll} A^i_\alpha x_{\alpha\beta} & = 0 \\ B^i_\beta A^i_\alpha x_{\alpha\beta} & \equiv 0 \end{array}\right\} \qquad \begin{array}{r} 1\ 2^i \\ 1\ 3^i \end{array}$$

has one point common with the $[q-2]$

$$\left.\begin{array}{ll} B^j_\beta x_{\alpha\beta} & = 0 \\ A^j_\beta B^j_\alpha x_{\alpha\beta} & \equiv 0 \end{array}\right\} \qquad \begin{array}{r} 1\ 6^j \\ 1\ 3^j \end{array}$$

Since the spaces lie in a $[p+q-3]$ it is only necessary to show that there is one further relation connecting the left-hand sides of the $p+q$ equations 1.2^i and 1.6^j. This is —

$$B^j_\beta A^i_\alpha x_{\alpha\beta} \equiv A^i_\alpha B^j_\beta x_{\alpha\beta} \qquad 1.7$$

If the set B^j_β is actually that determined by the A^i_α, that is, is the same as the B^i_β, the identity 1.7 is implied in 1.3^i and 1.3^j (these, although now formally the same, modify different sets of equations, and so count as separate identities). There can be no identity to replace this one that is lost, so that a $[p-2]$ and a $[q-2]$ which are associated do not meet.

The number of $[p-2]$s given by 1.2 and 1.3 is the number of independent solutions of the equations 1.5, namely* $\dfrac{(p+q-2)!}{(p-1)!\,(q-1)!}$.

2. *The double-*N *of* $[p-2]$*s and* $[q-2]$*s in* $[p+q-3]$ *has in general no quadric w.r. to which it is self-polar.*

The proof of the non-existence of the Schur quadric for the general (self-dual) double-N is complicated by the existence of one for special values of p and q, viz., $p=2$, q arbitrary, and $p=q=3$. It is effected in three stages, p is assumed $\leqslant q$, and it is then shown that —

(1) If in $[p+q-3]$, p arbitrary $[p-2]$s are taken, and p $[q-2]$s drawn, each of which meets a different set of $p-1$ of the $[p-2]$s, but has no other specialization, then a double-N of $[p-2]$s and $[q-2]$s can be found, which contains these two sets of p spaces, i.e., a double-N can be found, among whose spaces are those of an arbitrary double-p.

(2) For given p (other than 2), and q between 3 and some greater number depending on p, no quadric can be constructed w.r. to which a general double-p of $[p-2]$s and $[q-2]$s in $[p+q-3]$ is self-polar, and therefore in consequence of 2.1, for such p, and q, there can be no quadric w.r. to which a double-N, among whose spaces are those of the double-p, is self-polar.

(3) The existence of a Schur quadric for the double-N′ of $[p-2]$s and $[q-1]$s in $[p+q-2]$, implies the existence of one for the double-N of $[p-2]$s and $[q-2]$s in $[p+q-3]$, i.e., if for given p, and some q, there is no Schur quadric, then there is none for that p, and any greater q.

Since we have only a negative proposition to prove, it does not matter if the double-N obtained in 2.1 is in some way specialized (and although not proved, it is actually fairly clear that this is not so), for specialization would merely involve some relations between the $a_{\alpha\beta}$. The coefficients in the equation of the Schur quadric, if it exists, are functions of the $a_{\alpha\beta}$ only, and thus if none exists when these are related, certainly none can when these restrictions are removed. In 2.2, therefore, it is actually proved that for given p, and a certain range of q, there is no Schur quadric, for the general (self-dual) double-N. 2.3 then shows that there is no Schur quadric at all, except in a few very special cases.

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* Segre, 'Encykl. der Math. Wiss.,' III, c. 7, p. 826.

2.1 *A double-*N *can be constructed which contains the spaces of a given double-p of $[p-2]$s and $[q-2]$s in $[p+q-3]$.*

Every $[p-2]$ which meets a $[q-2]$ lies with it in a $[p+q-4]$. There are $p-1$ independent $[p+q-4]$s of this sort passing through each of the $[q-2]$s of a double-p and, the space being of dimension $p+q-3$, the $[q-2]$s therefore are completely defined by these. Each of the $[p-2]$s has also to lie in $p-1$ of these $[p+q-4]$s, but beyond this is so far arbitrary. We can suppose each of them defined by $q-p$ further $[p+q-4]$s. Thus we can take for the equations of the $[q-2]$s of a double-p

$$\left.\begin{array}{l} y_{21} = y_{31} = \dots = y_{p1} = 0 \\ y_{12} = y_{32} = \dots = y_{p2} = 0 \\ \quad \cdot \quad \cdot \quad \cdot \\ y_{1p} = y_{2p} = y_{3p} = \dots = y_{\overline{p-1}\,p} = 0 \end{array}\right\} \qquad 2.1.1$$

and for those of the $[p-2]$s

$$\left.\begin{array}{l} y_{12} = y_{13} = \dots = y_{1p} = y_{1\,\overline{p+1}} = \dots = y_{1q} = 0 \\ y_{21} = y_{23} = \dots = y_{2p} = y_{2\,\overline{p+1}} = \dots = y_{2q} = 0 \\ \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ y_{p1} = y_{p2} = y_{p3} = \dots = y_{p\,\overline{p-1}} = y_{p\,\overline{p+1}} = \dots = y_{pq} = 0 \end{array}\right\} \qquad 2.1.2$$

where the $y_{\alpha\beta}$ are linear functions of the co-ordinates in the $[n]$ of the form

$$\text{and} \qquad \left.\begin{array}{ll} y_{\alpha\beta} = b_{\alpha\beta\epsilon}x_{\epsilon} & (\alpha \neq \beta) \\ \quad \equiv 0 & (\alpha = \beta) \end{array}\right\} \quad \begin{array}{l} \alpha = 1, \dots p \\ \beta = 1, \dots q \\ \epsilon = 1, \dots n+1 \end{array}$$

The equations

$$A_{\alpha}y_{\alpha\beta} = 0 \qquad 2.1.3$$

for which quantities B_{β} can be found, such that

$$B_{\beta}A_{\alpha}y_{\alpha\beta} \equiv 0 \qquad 2.1.4$$

are those of the $[p-2]$s of a double-N. Among the sets of A_{α} which make 2.1.4 possible are those in which all but one of them, say all but A_1, are zero. Then, since $y_{11} = 0$, there are only $q-1$ equations in the family 2.1.3, viz. :—

$$y_{12} = y_{13} = \dots = y_{1q} = 0.$$

and 2 1.4 is satisfied when all the B_β but B_1 are zero Among the $[p \quad 2]$s of this double-N, then, are those of the double-p Similarly, we see that the $[q-2]$s of the double-p are among those of the same double-N

Alternatively, the equations of a double-N can be reduced from their general form to this, which gives explicit equations for the spaces of the double-p obtained from any p of its $[p-2]$s and their associated $[q-2]$s For, any of the q equations

$$A_\alpha x_{\alpha\beta} = 0 \qquad 1.2$$

can be replaced by the sum of linear multiples of the whole family, *i e*, we could replace the whole family by

$$C_{\beta\beta'} A_\alpha x_{\alpha\beta'} = 0, \qquad \beta' = 1, \quad q$$

or

$$A_\alpha (C_{\beta\beta'} x_{\alpha\beta'}) = 0$$

(summation over the α and β') where the $C_{\beta\beta'}$ are any q^2 constants Further, the whole configuration of $[p-3]$s represented by the equations 1.2, without the identical relation, and therefore of $[p-2]$s contained in it, is unaltered if, instead of the original equations, we write —

$$D_{\alpha\alpha} A_\alpha x_{\alpha\beta} = 0$$

(summation over the α, and the α'), the $D_{\alpha\alpha'}$ being any p^2 constants So that, altogether, the family of $[p-2]$s may be represented by

$$A_\alpha (C_{\beta\beta'} D_{\alpha\alpha} x_{\alpha'\beta}) = 0 \qquad 2\ 1\ 6$$

where some identical relation corresponding to 1 3 still connects the left-hand sides Now suppose that each set of $D_{1\alpha}, D_{2\alpha}, \quad D_{p\alpha'}$ is equal to a different set of A_α, which, inserted in the equations

$$A_\alpha x_{\alpha'\beta'} = 0,$$

gives a $[p-2]$, and that $C_{1\beta'}$, $C_{2\beta'}$, $C_{p\beta'}$ are the corresponding sets of B_β (the remaining $C_{\beta\beta'}$ can be taken arbitrarily) Then —

$$C_{\beta\beta'} D_{\alpha\alpha} x_{\alpha\beta'} \equiv 0, \quad \text{for} \quad \alpha = \beta$$

Writing

$$y_{\alpha\beta} = C_{\beta\beta'} D_{\alpha\alpha'} x_{\alpha\beta'},$$

the equations have been reduced to the required form

It may be proved that there are no relations connecting the $C_{\beta\beta'} D_{\alpha\alpha'} a_{\alpha'\beta'\epsilon}$ $(= b_{\alpha\beta\epsilon})$, and, consequently, that the double-p obtained from any p of the spaces of either family of the double-N is no less general than that constructed originally

2 2 ***For any p there is a range of values of q for which the general double-p of [p − 2]s and [q − 2]s in [p + q − 3] has no quadric w r to which it is self-polar***

The freedom of a quadric in $[p+q-3]$ is reduced by $(p-1)\ (q-1)$ if a given $[p-2]$ and $[q-2]$ are made to be polars Two such pairs reduce the freedom by twice that number, except if the second $[p-2]$ meets the first $[q-2]$, in which case the second $[q-2]$ will have to meet the first $[p-2]$, for a non-degenerate quadric to exist at all, and then, if the incidence is in a point only, the reduction is one less than that In this way it is seen that for a double-p to have a quadric w r to which it is self-polar, it must be possible to make the quadric satisfy

$$p\,(p-1)\,(q-1)-\tfrac{1}{2}p\,(p-1)$$

conditions But the freedom of quadrics in $[p+q-3]$ is

$$\tfrac{1}{2}\,(p+q)\,(p+q-3),$$

and therefore for a quadric to be possible, we must have

$$(p+q)\,(p+q-3) \geqslant p\,(p-1)\,(2q-3) \qquad 2\ 2\ 1$$

This requires that q shall not lie between

$$\tfrac{1}{2}\,\{2p^2-4p+3 \pm \sqrt{(2p^2-4p+3)^2-16p^2+24p}\} \qquad 2\ 2\ 2$$

or

$$(p-1)^2+\tfrac{1}{2}\pm\left\{p^2\,(p-1)\,(p-3)+\frac{9}{4}\right\}^{\frac{1}{2}}$$

(but may take either of these two values if it is integral) There are, therefore, three cases —

(*a*) $p=2$ The inequality 2 2 1 is always satisfied, and a quadric can be found w r to which the double-p, which is just two $[n-1]$s and two points, one lying in each, is self-polar The double-N is the simplex in $[n]$, and this is known to have a quadric w r to which it is self-polar

(*b*) $p=3$ When $q=3$, 2 2 1 is an equality, the double-p is a skew hexagon, and the double-N is the double-six, and both these have a Schur quadric, but 2 2 1 is not satisfied again until $q \geqq 6$

(*c*) $p>3$. The lower value of the expression for q is less than 3, and thus, since $q \geqq p$, is not significant, whilst the upper value is certainly greater than p^2.

2 3 *If there is no Schur quadric for the double-*N *of* $[p-2]$*s and* $[q-2]$*s in* $[p+q-3]$, *there can be none for the double-*N′ *of* $[p-2]$*s and* $[q-1]$*s in* $[p+q-2]$

Take as co-ordinates in the $[p+q-2]$ $x_1, x_2,$ x_{p+q-2}, and x_0, and consider first the whole ∞^{p-1} family of $[p-3]$s given by the $q+1$ equations —

$$\left.\begin{aligned} A_\alpha(x_{\alpha\beta}+a_{\alpha\beta0}x_0) &= 0 \\ A_\alpha(x_{\alpha0}+a_{\alpha00}x_0) &= 0 \end{aligned}\right\} \qquad \begin{aligned} \alpha &= 1, \quad p, \\ \beta &= 1, \quad q, \end{aligned} \tag{2 3 1}$$

in which the $x_{\alpha\beta}$ and the $x_{\alpha0}$ are linear functions of the co-ordinates $x_1, x_2,$. x_{p+q-2}, but not x_0, of the form

$$\left.\begin{aligned} x_{\alpha\beta} &= a_{\alpha\beta\epsilon}x_\epsilon \\ x_{\alpha0} &= a_{\alpha0\epsilon}x_\epsilon \end{aligned}\right\} \qquad \epsilon = 1, \quad p+q-2, \tag{2 3 2}$$

and the A_α take all possible values Suppose that the $a_{\alpha\beta0}$ are not general, but connected by the pq relations

$$a_{\alpha\beta0} = k_\beta a_{\alpha00} \tag{2 3 3}$$

where the k_β are q given constants Then ∞^{p-2} of the $[p-3]$s pass through the point x_0, for the only condition required for this is that the A_α should satisfy the single linear relation

$$A_\alpha a_{\alpha00} = 0 \tag{2 3.4}$$

Project the figure from this point on to the $[p+q-3]$, $x_0 = 0$ The equations of the projected figure are obtained by eliminating the x_0 from the equations 2 3 1, and are therefore, by subtracting λ_β times the last equation from the βth of the family,

$$A_\alpha(x_{\alpha\beta} - k_\beta x_{\alpha0}) = 0 \tag{2.3 5}$$

Included in the family of $[p-3]$s represented by the equations 2 3 1, there is a finite number of $[p-2]$s, occurring when the A_α are such that quantities $B_1, B_2,$ B_q, and B_0 can be found for which

$$B_\beta A_\alpha(x_{\alpha\beta}+a_{\alpha\beta0}x_0) + B_0A_\alpha(x_{\alpha0}+a_{\alpha00}x_0) \equiv 0, \tag{2 3 6}$$

i.e.,

$$\left.\begin{aligned} B_\beta A_\alpha a_{\alpha\beta\epsilon} + B_0A_\alpha a_{\alpha0\epsilon} &= 0 \\ B_\beta A_\alpha a_{\alpha\beta0} + B_0A_\alpha a_{\alpha00} &= 0 \end{aligned}\right\} \tag{2.3 7}$$

In consequence of 2.3 2 the last of these equations may be written,

$$(B_\beta\lambda_\beta + B_0)(A_\alpha a_{\alpha00}) = 0.$$

The $[p-2]$s therefore split into two families those for which

$$A_\alpha a_{\alpha 00} = 0$$

which pass through X_0 and those for which

$$B_\beta \lambda_\beta + B_0 = 0$$

which do not Taking the second family and substituting for B_0 in the remaining equations of 2 3 7 we get

$$B_\beta A_\alpha (a_{\alpha\beta\gamma} - \lambda_\beta a_{\alpha 0 \gamma}) = 0 \qquad 2\ 3\ 8$$

These equations are not different from 1 4 and the number of solutions when the B_β are eliminated in A_α is therefore $\dfrac{(p+q-2)!}{(p-1)!\,(q-1)!}$

Now consider the $[p-2]$s which do pass through X_0 They satisfy

$$\left.\begin{aligned} A_\alpha (B_\beta a_{\alpha\beta\gamma} + B_0 a_{\alpha 0 \gamma}) &= 0 \\ A_\alpha a_{\alpha 00} &= 0 \end{aligned}\right\} \qquad 2\ 3\ 9$$

equations formally the same as 1 4 with one more independent parameter B_β and one fewer independent parameters A_α and having therefore when the B_β are eliminated $\dfrac{(p+q-2)!}{(p-2)!\,q!}$ solutions in the A_α Thus of the $[p-2]$s of this double $\dfrac{(p+q-1)!}{(p-1)!\,q!}$ in $[p+q-2]$ $\dfrac{(p+q-2)!}{(p-2)!\,q!}$ pass through X_0 and the rest do not

The $[q-1]$s of the double N are represented by

$$B_\beta (x_{\alpha\beta} + a_{\alpha\beta 0} x_0) + B_0 (x_{\alpha 0} + a_{\alpha 00} x_0) = 0 \qquad 2\ 3\ 10$$

with the identical relation 2 3 6 The condition that one of these should pass through X_0 is

$$B_\beta a_{\alpha\beta 0} + B_0 a_{\alpha 00} = 0$$

i e

$$B_\beta \lambda_\beta + B_0 = 0$$

so that using equations 2 3 8 and 2 3 9 again we find that of the $\dfrac{(p+q-1)!}{(p-1)!\,q!}$ $[q-2]$s of the system $\dfrac{(p+q-2)!}{(p-1)!\,(q-1)!}$ pass through X_0 and the rest do not

When the double N is projected from X_0 on to $x_0 = 0$ we obtain two double configurations (*a*) a double $\dfrac{(p+q-2)!}{(p-1)!\,(q-1)!}$ of $[p-2]$s and $[q-2]$s derived from the $[p-2]$s of the original figure which do not pass through X_0, and the $[q-1]$s which do, this is represented by the equations

$$A_\alpha (x_{\alpha\beta} - k_\beta x_{\alpha 0}) = 0$$

and

$$B_\beta (x_{\alpha\beta} - k_\beta x_{\alpha 0}) = 0$$

where the A_α and B_β occur in pairs for which

$$A_\alpha B_\beta (x_{\alpha\beta} - k_\beta x_{\alpha 0}) \equiv 0\,,$$

and (*b*) a double-$\dfrac{(p+q-2)!}{(p-2)!\,q!}$ of $[p-3]$s and $[q-1]$s derived from the remaining $[p-2]$s and $[q-1]$s of the original figure, whose equations are

$$\left.\begin{aligned} A_\alpha x_{\alpha\beta} &= 0 \\ A_\alpha x_{\alpha 0} &= 0 \\ A_\alpha a_{\alpha 00} &= 0 \end{aligned}\right\}$$

and

$$B_\beta x_{\alpha\beta} + B_0 x_{\alpha 0} = 0,$$

where the A_α and B_β occur in pairs for which

$$A_\alpha B_\beta x_{\alpha\beta} + A_\alpha B_0 x_{\alpha 0} = 0$$

Suppose the general double-$\dfrac{(p+q-1)!}{(p-1)!\,q!}$ of $[p-2]$s and $[q-1]$s in $[p+q-2]$ has a quadric w r to which it is self-polar, then the particular configuration above has a quadric cone,* vertex, X_0, w r to which it is self-polar, and consequently both the configurations arising from the projection would be self-polar w r to some quadric If either of them is not, there could be no quadric in the $[p+q-2]$, and therefore no quadric for the general figure in $[p+q-2]$

Since no limitation has been placed on the $a_{\alpha\beta}$, and the $a_{\alpha\beta 0}$, the configurations in the $[p+q-3]$ are quite general double configurations of the sort under consideration Suppose that q is the greatest value for the given p which will not satisfy 2 2 1, then the double-N of $[p-2]$s and $[q-2]$s in $[p+q-3]$ has no Schur quadric, and therefore the double-N′ of $[p-2]$s and $[q-1]$s in $[p+q-2]$ has none, and so on, for all larger values of q

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* The argument down to this point may be applied to the case of the lines of a cubic surface which has a node The six lines through the node meet a plane in two triads of points of a conic, these two triads are both self-polar in regard to a proper conic of the plane.

3. *In space of n dimensions it is possible to find a family of* N *spaces of dimension* $r(p-r)-1$ *and a family of* N *spaces of dimension* $r(q-r)-1$ *such that each space of either family meets all but one of the spaces of the other.*

$$n = r(p+q-r) - 2, \quad p > r, \quad q > r$$

$$N = \frac{(p+q-2r)!\,(p+q-2r+1)! \ldots (p+q-r-1)!\ 1!\,2! \ldots (r-1)!}{(p-r)!\,(p-r+1)! \ldots (p-1)!\,(q-r)!\,(q-r+1)! \ldots (q-1)!}$$

Take as before $x_1, x_2, \ldots x_{n+1}$ as co ordinates in the $[n]$ and let $x_{11}, x_{12}, \ldots x_{\alpha\beta}, \ldots x_{pq}$ be pq arbitrary linear functions of them of the form

$$x_{\alpha\beta} = a_{\alpha\beta\epsilon} x_\epsilon \qquad \left.\begin{array}{l} \alpha = 1 \ldots p \\ \beta = 1 \ldots q \\ \epsilon = 1 \ldots n+1 \end{array}\right\} \qquad 1\,1$$

Now consider the q sets of r equations —

$$\left.\begin{array}{l} A_{11}x_{1\beta} + A_{21}x_{2\beta} + \ldots + A_{p1}x_{p\beta} = 0 \\ A_{12}x_{1\beta} + A_{22}x_{2\beta} + \ldots + A_{p2}x_{p\beta} = 0 \\ \ldots \\ A_{1r}x_{1\beta} + A_{2r}x_{2\beta} + \ldots + A_{pr}x_{p\beta} = 0 \end{array}\right\}$$

in which a set is characterised by the value of β; any one of the equations will be written as

$$A_{\alpha\gamma}x_{\alpha\beta} = 0 \qquad \gamma = 1 \ldots r \qquad 3\,2$$

in which the quantities $A_{\alpha\gamma}$ are at present arbitrary parameters. If these qr equations are to represent a $[r(p-r)-1]$ the $A_{\alpha\gamma}$ must be such that there is one linear identity connecting their left hand sides, i.e. such that quantities $B_{\beta\gamma}$ can be found for which

$$\begin{aligned} & B_{11}(A_{\alpha 1}x_{\alpha 1}) + B_{21}(A_{\alpha 1}x_{\alpha 2}) + \ldots + B_{q1}(A_{\alpha 1}x_{\alpha q}) \\ & \quad + B_{12}(A_{\alpha 2}x_{\alpha 1}) + B_{22}(A_{\alpha 2}x_{\alpha 2}) + \ldots + B_{q2}(A_{\alpha 2}x_{\alpha q}) \\ & \quad + \ldots \\ & \quad + B_{1r}(A_{\alpha r}x_{\alpha 1}) + B_{2r}(A_{\alpha r}x_{\alpha 2}) + \ldots + B_{qr}(A_{\alpha r}x_{\alpha q}) \equiv 0, \end{aligned}$$

i.e.

$$B_{\beta\gamma}A_{\alpha\gamma}x_{\alpha\beta} \equiv 0. \qquad 3\,3$$

This being an identity in the x_ϵ, is equivalent to the $n+1$ equations

$$B_{\beta\gamma}A_{\alpha\gamma}a_{\alpha\beta\epsilon} = 0 \qquad 3\,4$$

By eliminating the $B_{\beta\gamma}$ from these, we find the conditions that must be satisfied by the $A_{\epsilon\gamma}$ in order that the equations 3.2 may represent a $[r(p-r)-1]$, namely —

$$\left\| \begin{array}{llll} A_{\epsilon 1}a_{\epsilon 11}, & A_{\epsilon 1}a_{\epsilon 12}, & , & A_{\epsilon 1}a_{\epsilon 1\,\overline{n+1}} \\ A_{\epsilon 2}a_{\epsilon 11} & & & \\ & & & \\ A_{\epsilon r}a_{\epsilon 11} & & & \\ A_{\epsilon 1}a_{\epsilon 21} & & & \\ & & & \\ A_{\epsilon r}a_{\epsilon 21} & & & \\ & & & \\ A_{\epsilon r}a_{\epsilon q 1} & & & \end{array} \right\| = 0, \qquad 3.5$$

a matrix of $n+1$ columns and qr rows, in which all determinants of qr rows and columns vanish.

Alternatively, by eliminating the $A_{\epsilon\gamma}$ we should get the conditions satisfied by the $B_{\beta\gamma}$, namely, the vanishing of all determinants of pr rows and columns, in a matrix of pr rows and $n+1$ columns, whose general element is $(B_{\beta\gamma}a_{\alpha\beta\epsilon})$, in which the ϵ takes all values along any row, and the α and γ all pairs of values down any column. 3.6

Any set of $A_{\epsilon\gamma}$ which satisfies equations 3.5 determines uniquely, save for an arbitrary common multiplier, by means of equations 3.4, a set of $B_{\beta\gamma}$, which satisfies 3.6, i.e., any $[r(p-r)-1]$ given by the qr equations

$$A_{\alpha\gamma}x_{\alpha\beta} = 0, \qquad 3.2$$

in which the $A_{\alpha\gamma}$ are such that there is an identical relation connecting the left-hand sides, is associated with a unique $[r(q-r)-1]$ given by the equations

$$B_{\beta\gamma}x_{\alpha\beta} = 0, \qquad 3.7$$

the $B_{\beta\gamma}$ being also necessarily such that there is an identical relation connecting the left hand sides of these.

Before proceeding to find the actual number of possible distinct $[r(p-r)-1]$s, if finite, represented by the equations 3.2 and 3.5, it can be shown that these spaces form with the associated family of $[r(q-r)-1]$s a "double" configuration. That is, if $A'_{\epsilon\gamma}$ is one set of $A_{\epsilon\gamma}$ satisfying equations 3.5, and $B'_{\beta\gamma}$

any set of $B_{\beta\gamma}$ satisfying equations 3 6, except that which with $A^i_{\alpha\gamma}$ satisfies 3 4, then the $[r(p-r)-1]$

$$\left.\begin{aligned} A^i_{\alpha\gamma}x_{\beta\gamma} &= 0 \qquad 3\ 2^i \\ B^i_{\beta\gamma}A^i_{\alpha\gamma}x_{\alpha\beta} &= 0 \qquad 3\ 3^i \end{aligned}\right\}$$

has one point common with the $[r(q-r)-1]$

$$\left.\begin{aligned} B^j_{\beta\gamma}x_{\alpha\beta} &= 0 \qquad 3\ 7^j \\ A^j_{\alpha\gamma}B^j_{\beta\gamma}x_{\alpha\beta} &\equiv 0 \qquad 3\ 3^j \end{aligned}\right\}$$

Since both these spaces lie in a $[r(p+q-r)-2]$ it is only necessary to show that there are r^2 further identical linear relations connecting the left-hand sides of 1 2^i and 3 7^j These relations are —

$$B^j_{\beta 1}A^i_{\alpha 1}x_{\alpha\beta} - A^i_{\alpha 1}B^j_{\beta 1}x_{\alpha\beta} \equiv 0$$
$$B^j_{\beta 2}A^i_{\alpha 1}x_{\alpha\beta} - A^i_{\alpha 1}B^j_{\beta 2}x_{\alpha\beta} \equiv 0, \text{ etc}$$

The general relation of this family is —

$$B^j_{\beta\gamma_j}\,A^i_{\alpha\gamma_i}x_{\alpha\beta} - A^i_{\alpha\gamma_i}B^j_{\beta\gamma_j}x_{\alpha\beta} \equiv 0 \qquad 3\ 8$$

(there being no summation over the γ_i and γ_j) and all pairs of γ_i and γ_j (both ranging from 1 to r) give rise to distinct identities Thus, any space of either family meets but one of the spaces of the other, it has now to be shown that it does not meet the last that is, that the $[r(p-r)-1]$ given by the set $A^i_{\alpha\gamma}$ does not meet the $[r(q-r)-1]$ given by the set $B^i_{\beta\gamma}$ This is true if the number of independent identities in the family 3 8 is fewer than r^2 since no identical relations can hold here without their holding in the case considered above (The relations 3 3^i and 3 3^j, although now the same, modify different sets of equations and so count separately) Of the r relations of the family 3 8, obtained when $\gamma_i = \gamma_j$ all but one now implies the last, in consequence of 3 3^i This is the relation that is lost The two families of spaces represented by

$$A_{\alpha\gamma}x_{\alpha\beta} = 0$$

and

$$B_{\beta\gamma}x_{\alpha\beta} = 0$$

where the $A_{\alpha\gamma}$ and the $B_{\beta\gamma}$ occur in pairs for which

$$A_{\alpha\gamma}B_{\beta\gamma}x_{\alpha\beta} \equiv 0$$

form therefore a double N.

The calculation of the number N presents rather more difficulty in this case, since any one of the equations of a set

$$A_{\alpha\gamma}x_{\alpha\beta} = 0 \qquad 3.2$$

may be replaced by the sum of linear multiples of the whole set of r, having the same β—that is, by

$$P_{\gamma}A_{\alpha\gamma}x_{\alpha\beta} = 0$$

Thus, several sets of $A_{\alpha\gamma}$ give equations which represent the same space. We want therefore to find sets of functions of the $A_{\alpha\gamma}$, each of which corresponds uniquely to a $[r(p-r)-1]$. Such functions are

$$K_{\alpha\beta} = A_{\alpha\gamma}B_{\beta\gamma} \tag{3.9}$$

These satisfy the $n+1$ equations

$$K_{\alpha\beta}a_{\alpha\beta i} = 0, \tag{3.10}$$

and, further, a number of relations among them is involved in the equations 3.9, when the $A_{\alpha\gamma}$ and the $B_{\beta\gamma}$ are eliminated. Eliminating first the $B_{\beta\gamma}$, we get the q sets of equations

$$\left\| \begin{matrix} K_{1\beta}, & A_{11}, & A_{12}, & , A_{1r} \\ K_{2\beta}, & A_{21}, & A_{22}, & , A_{2r} \\ & & & \\ K_{p\beta}, & A_{p1}, & A_{p2}, & , A_{pr} \end{matrix} \right\| = 0 \tag{3.11}$$

in which each column after the first is the same for all the q sets of equations. The $K_{\alpha\beta}$ are actually, therefore, functions of the determinants of r rows and columns in the array

$$\left\| \begin{matrix} A_{11}, & , A_{1r} \\ & \\ A_{p1}, & , A_{pr} \end{matrix} \right\| \text{ only}$$

But the two $[r(p-r)-1]$s represented by the equations

$$\left.\begin{aligned} A'_{\alpha\gamma}x_{\alpha\beta} &= 0 \\ B'_{\beta\gamma}A'_{\alpha\gamma}x_{\alpha\beta} &\equiv 0 \end{aligned}\right\} \qquad \begin{aligned} &3.2' \\ &3.3' \end{aligned}$$

and

$$\left.\begin{aligned} A''_{\alpha\gamma}x_{\alpha\beta} &= 0 \\ B''_{\alpha\gamma}A''_{\beta\gamma}x_{\alpha\beta} &\equiv 0 \end{aligned}\right\} \qquad \begin{aligned} &2.3'' \\ &3.3'' \end{aligned}$$

respectively can only coincide if quantities $P''_{\gamma\gamma'}$ and $P''_{\gamma\gamma''}$ can be found for which

$$P'_{\gamma\gamma'}A'_{\alpha\gamma} = P''_{\gamma\gamma''}A''_{\alpha\gamma''}, \quad \gamma, \ \gamma', \ \gamma'' = 1, \dots r$$

(summation over the γ', and over the γ'') for all α and γ This is a sufficient condition for

$$\begin{Vmatrix} A'_{11}, & , A'_{1r} \\ \\ A'_{p1} & , A'_{pr} \end{Vmatrix} = \begin{Vmatrix} A''_{11}, & , A'_{1r} \\ \\ A''_{p1}, & , A'_{pr} \end{Vmatrix}$$

the equality extending to all corresponding minors of r rows and columns Thus if two sets of $A_{\alpha\gamma}$ lead to the same $[r(p-r)-1]$, they also give rise to the same equations for determining the $K_{\alpha\beta}$ and the ratios of these are therefore determined uniquely for each $[r(p-r)-1]$

Conversely, we can start with a set of $K_{\alpha\beta}$ (supposed suitable) and show that it leads to a unique $[r(p-r)-1]$ Take the equations of the family 3 11 obtained for $\beta = 1$ and 2, viz –

$$\begin{Vmatrix} K_{11} & A_{11}, & A_{1r} \\ \\ K_{p1} & A_{p1} & A_{pr} \end{Vmatrix} = 0 \qquad 3\ 11_1$$

and

$$\begin{Vmatrix} K_{12} & A_{11} & A_{1r} \\ \\ K_{p2}, & A_{p1} & , A_{pr} \end{Vmatrix} = 0 \qquad 3\ 11_2$$

Since not all the determinants of r rows and columns in the $A_{\alpha\gamma}$ can vanish (as then of each set of r equations in 3 2, $r-1$ only would be independent, and this implies some limitation on the $a_{\alpha\beta\epsilon}$), these two families of equations involve the vanishing of all determinants of $r+1$ rows and columns in

$$\begin{vmatrix} K_{11} & K_{12}, & A_{11}, & , A_{1r} \\ \\ K_{p1}, & K_{p2} & A_{p1}, & , A_{pr} \end{vmatrix}$$

Repeating this process, giving β all its values, it is seen that all determinants of $r+1$ rows and columns in

$$\begin{Vmatrix} K_{11}, & K_{12}, & , K_{1q}, & A_{11}, & , A_{1r} \\ \\ K_{p1}, & K_{p2}, & , K_{pq}, & A_{p1}, & A_{pr} \end{Vmatrix} \qquad 3\ 12$$

vanish

In particular, we have the r sets of equations

$$\left\| \begin{matrix} \mathrm{K}_{11}, & \quad , \mathrm{K}_{1r}, & \mathrm{A}_{1\gamma} \\ & \cdot & \\ \mathrm{K}_{p11} & \quad , \mathrm{K}_{pr}, & \mathrm{A}_{p\gamma} \end{matrix} \right\| = 0 \tag{3.13}$$

Since, in consequence of the necessary relations between the $\mathrm{K}_{\alpha\beta}$, other similar sets of equations in the same $\mathrm{A}_{1\gamma}, \quad , \mathrm{A}_{p\gamma}$ are not distinct from these, the complete set of conditions governing the $\mathrm{A}_{\alpha\gamma}$, for each γ, may be written in the form

$$\left.\begin{aligned} k_{11}\mathrm{A}_{1\gamma} + k_{12}\mathrm{A}_{2\gamma} + \quad &+ k_{1\,\overline{r+1}}\mathrm{A}_{\overline{r+1}\,\gamma} = 0 \\ k_{22}\mathrm{A}_{2\gamma} + k_{23}\mathrm{A}_{3\gamma} + \quad &+ k_{2\,\overline{r+2}}\mathrm{A}_{\overline{r+2}\,\gamma} = 0 \\ & \\ k_{\overline{p-r}\,\overline{p-r}}\mathrm{A}_{\overline{p-r}\,\gamma} + \quad &+ k_{\overline{p-r}\,p}\mathrm{A}_{p\gamma} \quad = 0 \end{aligned}\right\} \tag{3.14}$$

where the $k_{11}, \quad , k_{\overline{p-r}\,p}$ are determinants formed from the $\mathrm{K}_{\alpha\beta}$ Consider the family of equations comprising the first of the sets 3 14 for each γ, namely,

$$\left.\begin{aligned} k_{11}\mathrm{A}_{11} + k_{12}\mathrm{A}_{21} + \quad &+ k_{1\,\overline{r+1}}\mathrm{A}_{\overline{r+1}\,1} = 0 \\ k_{11}\mathrm{A}_{12} + k_{12}\mathrm{A}_{22} + \quad &+ k_{1\,\overline{r+1}}\mathrm{A}_{\overline{r+1}\,2} = 0 \\ &\cdot \\ k_{11}\mathrm{A}_{1r} + k_{12}\mathrm{A}_{2r} + \quad &+ k_{1\,\overline{r+1}}\mathrm{A}_{\overline{r+1}\,r} = 0 \end{aligned}\right\} \tag{3.15$_1$}$$

Add to this family the equation

$$k_{11}l_1 + k_{12}l_2 + \quad k_{1\,\overline{r+1}}l_{\overline{r+1}} = 0 \tag{3.16$_1$}$$

where the l are arbitrary, beyond satisfying this equation. Then constants $p_1, \quad , p_\gamma, \quad , p_r$ can be found uniquely, such that

$$\left.\begin{aligned} p_\gamma\mathrm{A}_{1\gamma} &= l_1 \\ & \\ p_\gamma\mathrm{A}_{\overline{r+1}\,\gamma} &= l_{\overline{r+1}} \end{aligned}\right\} \tag{3.17$_1$}$$

Now take the family of equations comprising the second of the sets 3 14 for each γ, and add to it the equation

$$k_{22}l_2 + k_{23}l_3 + \quad + k_{2\,\overline{r+2}}l_{\overline{r+2}} = 0 \tag{3.16$_2$}$$

(l_{r+2} is therefore determinate in terms of the rest). Then for the same p_γ as above, we have in addition the equation

$$p_\gamma\mathrm{A}_{\overline{r+2}\,\gamma} = l_{\overline{r+2}} \tag{3.17$_2$}$$

Similarly, generally, for all $\alpha = l, \qquad p$

$$p_\gamma A_{\alpha\gamma} = l_\alpha \tag{3 17}$$

wherein, of the l_α, r are arbitrary, and the rest determinable from them in terms of the $l_{11}, \quad l_{\overline{p-r}\,p}$, by means of equations 3 16 Thus, if $A'_{\alpha\gamma}$ and $A''_{\alpha\gamma}$ are two sets of $A_{\alpha\gamma}$ derived from the same set of $K_{\alpha\beta}$, constants p'_γ and p''_γ depending on the $A'_{\alpha\gamma}$, $A''_{\alpha\gamma}$, and l_α can always be found so that

$$p'_\gamma A''_{\alpha\gamma} = l_\alpha - p''_\gamma A_{\alpha\gamma}$$

for all α Each distinct set of l_α gives rise to distinct sets of p'_γ and p''_γ, and there are r independent sets of l_α This is exactly the condition that all sets of $A_{\alpha\gamma}$ derivable from a given set of $K_{\alpha\beta}$ should give equations which represent the same $[r(p-r)-1]$

Having found that the $[r(p-r)-1]$ derivable from a set of $K_{\alpha\beta}$ is unique, we can reduce its equations to a simpler form, assigning the values of certain of the $A_{\alpha\gamma}$, and find the rest in terms of the $K_{\alpha\beta}$. By adding together suitable multiples of the r equations

$$A_{\alpha\gamma} x_{\alpha\beta} = 0, \tag{3.2}$$

in which β is fixed, we can obtain an equivalent set of equations

$$A^0_{\alpha\gamma} x_{\alpha\beta} = 0, \tag{3 2^0}$$

in which

$$A^0_{\alpha\gamma} = 0 \quad \text{for} \quad \alpha - \gamma < 0, \quad \text{and} \quad \alpha - \gamma > p - r$$

and $\qquad = 1 \quad \text{for} \quad \alpha - \gamma = 0$

but are otherwise unspecialized Then the matrix 3.12, whose minors of $r+1$ rows and columns vanish, becomes

$$\left\| \begin{array}{llllll} K_{11}, & , K_{1q}, & 1, & 0, & , 0, & 0 \\ K_{21}, & , K_{2q}, & A^0_{21}, & 1, & , 0, & 0 \\ & & & \cdot & & \\ K_{r1}, & , K_{rq}, & A^0_{r1}, & A^0_{r2}, & , A^0_{r\,\overline{r-1}}, & 1 \\ K_{\overline{r+1}\,1}, & , K_{\overline{r+1}\,q}, & A^0_{\overline{r+1}\,1}, & A^0_{\overline{r+1}\,2}, & , A^0_{\overline{r+1}\,\overline{r-1}}, & A_{\overline{r+1}\,r} \\ & & & & & \\ K_{\overline{p-r+1}\,1}, & , K_{\overline{p-r+1}\,q}, & A^0_{\overline{p-r+1}\,1}, & A^0_{\overline{p-r+1}\,2}, & , A^0_{\overline{p-r+1}\,\overline{r-1}}, & A^0_{\overline{p-r+1}\,r} \\ K_{\overline{p-r+2}\,1}, & , K_{\overline{p-r+2}\,q}, & 0, & A^0_{\overline{p-r+2}\,2}, & , A^0_{\overline{p-r+2}\,\overline{r-1}}, & A^0_{\overline{p-r+2}\,r} \\ & & \cdot & & & \\ K_{p1} & , K_{pq}, & 0, & 0, & , 0, & A^0_{pr} \end{array} \right\|$$

a matrix in which each of the $A^0_{\alpha\gamma}$ columns contains $r-1$ zero elements and one unit element All the minors necessary can be selected from those containing only one column of $A^0_{\alpha\gamma}$, and that with only two non-zero elements, one of which is unity All the $A^0_{\alpha\gamma}$ are thus uniquely determinable in terms of the $K_{\alpha\beta}$ — *i e*, the equations of a $[r(p-r)-1]$ in this special form can be written in terms of the $x_{\alpha\beta}$ and $K_{\alpha\beta}$ only All the work of this section holds equally well for the $[r(q-r)-1]$s, using the $B_{\beta\gamma}$ instead of the $A_{\alpha\gamma}$

To each set of values of $K_{\alpha\beta}$ corresponds exactly one $[r(p-r)-1]$, and one $[r(q-r)-1]$, and any of those spaces gives rise to a unique set of ratios of $K_{\alpha\beta}$, so that the number of possible $[r(p-r)-1]$s represented by the equations

$$A_{\alpha\gamma}x_{\alpha\beta}=0 \tag{3 2}$$

in which the $A_{\alpha\gamma}$ are such that there is an identical relation connecting the left-hand sides, is equal to the number of solutions in $K_{\alpha\beta}$ of the equations

$$K_{\alpha\beta}=A_{\alpha\gamma}B_{\beta\gamma} \tag{3 9}$$

when the $A_{\alpha\gamma}$ and $B_{\beta\gamma}$ have been eliminated, the $K_{\alpha\beta}$ being also connected by $n+1$ linear relations The elimination of the $A_{\alpha\gamma}$ and $B_{\beta\gamma}$ leads to those equations of the family 3 12 which do not contain $A_{\alpha\gamma}$, namely, the equations obtained by the vanishing of the minors of $r+1$ rows and columns in

$$\begin{Vmatrix} K_{11}, & , & K_{1q} \\ \cdot & & \cdot \\ K_{p1}, & , & K_{pq} \end{Vmatrix} \tag{3 18}$$

$(p-r)(q-r)$ of these equations are independent, so that the $K_{\alpha\beta}$ are on the whole subject to $pq-1$ conditions, and their ratios are therefore just determinate The number of solutions of the equations 3 18 is known to be N *

Note—It will be seen that the determinant theorem involved is that a matrix of p rows and q columns, whereof every determinant of $r+1$ rows and columns vanishes ($r<p$, $r<q$), may be regarded as obtained by multiplying a matrix, A, of p rows and r columns into a matrix, B, of r rows and q columns, the elements in A, B being arbitrary to the extent involved in the possibility of replacing the columns of A by linear functions of themselves, with a corresponding replacement for the rows of B.

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* *Cf* Segre, 'Encyk. der Math. Wiss.,' vol. 3, c. 7, p. 828.

Relativity Quantum Mechanics with an Application to Compton Scattering

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§ 1. *Introduction*

The new quantum mechanics, introduced by Heisenberg[*] and since developed from different points of view by various authors,[†] takes its simplest form if one assumes merely that the dynamical variables are numbers of a special type (called q-numbers to distinguish them from ordinary or c-numbers) that obey all the ordinary algebraic laws except the commutative law of multiplication, and satisfy instead of this the relations

$$\left.\begin{aligned} q_r q_s - q_s q_r &= 0, \qquad p_r p_s - p_s p_r = 0 \\ q_r p_s - p_s q_r &= 0 \ (r \neq s) \text{ or } ih \ (r = s) \end{aligned}\right\} \tag{1}$$

where the p's and q's are a set of canonical variables and h is a c-number equal to $(2\pi)^{-1}$ times the usual Planck's constant. Equations (1) may be regarded as replacing the commutative law of the classical theory, as one can, with their help, build up a complete algebraic theory of quantities that are analytic functions of a set of canonical variables. Further, it may easily be seen that the quantity $[x, y]$ defined by

$$xy - yx = ih[x, y] \tag{2}$$

is completely analogous to the Poisson bracket of the classical theory. By means of this analogy the whole of the classical dynamical theory, in so far as it can be expressed in terms of P.B.'s instead of differential coefficients, may be taken over immediately into the quantum theory.

It has been shown by the author[‡] that the quantum solution of a multiply periodic dynamical system may be effected, as on the classical theory, by the introduction of uniformising variables, J's and w's, and the results can then be interpreted in a way of which the following is a brief outline. The total polarisation of the system can be expanded as a Fourier series in the w's whose coefficients are functions of the J's only On the classical theory, if one takes one of these coefficients, say, that of $e^{i(\alpha w)}$ where $(\alpha w) = \Sigma\alpha_r w_r$ and the α's are integers, and substitutes in it for the J_r a set of numbers, κ_r, say, the number thus obtained will determine the intensity of the $e^{i(\alpha w)}$ component of the radiation emitted by the system when in the state fixed by the equations $J_r = \kappa_r$ On the quantum theory, however, an ambiguity arises, since in the Fourier expansion of the polarisation the coefficients may be either in front of or behind their respective exponentials The $e^{i(\alpha w)}$ term, for instance, would be

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[*] Heisenberg, 'Zeits. f. Phys.,' vol. 33, p. 879 (1925).

[†] Born and Jordan, 'Zeits. f. Phys.,' vol. 34, p. 858 (1925); Born, Heisenberg and Jordan, 'Zeits. f. Phys.,' vol. 35, p. 557 (1926); Kramers, 'Physica,' vol. 5, p. 369 (1925); Dirac, 'Roy. Soc. Proc.,' A, vol. 109, p. 642 (1925); Born and Wiener, 'Zeits. f. Phys.,' vol. 36, p. 174 (1926) *or* 'Jour. Math. Phys. Mass.,' vol. 5, p. 84 (1926).

[‡] 'Roy. Soc. Proc.,' A, vol. 110, p. 561 (1926).

$$\tfrac{1}{2}C_\alpha e^{i(\alpha w)} = \tfrac{1}{2}e^{i(\alpha w)}C_\alpha',$$

where C_α and C_α' are in general two different functions of the J's, so that if one substitutes for the J_r the values κ_r, where the κ's are a set of c-numbers that may be regarded as fixing a stationary state of the system, one would obtain two $e^{i(\alpha w)}$ intensities related to this state. If, now, one puts

$$J_r e^{i(\alpha w)} = e^{i(\alpha w)} J_r',$$

then C_α must be the same function of the J's that C_α' is of the J''s, so that if one substituted for the J_r in C_α the values κ_r, one would obtain the same result (a c-number, of course) as if one substituted for the J_r in C_α' their values given by the equations $J_r' = \kappa_r$, and one may therefore suppose this result to determine the intensity of a component of the emitted radiation that is symmetrically related to the two states of the system given by $J_r = \kappa_r$ and $J_r' = \kappa_r$ It may be shown that $J_r' = J_r + \alpha_r h$, and hence the two states are respectively the initial and final states on Bohr's theory It may also be shown that the system has transition frequencies related to pairs of states as on Bohr's theory

It now remains only to determine what values one shall assume the κ's to take, and this may require an appeal to physical considerations For the case of the simple harmonic oscillator it has been shown rigorously by Born and Jordan* that the action variable can take only a certain discrete set of values, one of which gives a state of lowest energy, and their method seems to be capable of extension For the case of Compton scattering by a free electron, considered in the present paper, there is no restriction on the values that the action variable can take The initial value of the action variable is now determined by the initial velocity of the electron, which must, of course, be given from physical considerations

It will be observed that the notion of canonical variables plays a very fundamental part in the theory Any attempt to extend the domain of the present quantum mechanics must be preceded by the introduction of canonical variables into the corresponding classical theory, with a reformulation of this classical theory with P.B 's instead of differential coefficients The object of the present paper is to obtain in this way the extension of the quantum mechanics to systems for which the Hamiltonian involves the time explicitly (§ 2) and to relativity mechanics (§§ 3, 4)

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* Born and Jordan, *loc. cit.*, § 5.

§ 2 *Quantum Time*

Consider a dynamical system of u degrees of freedom for which the Hamiltonian H involves the time explicitly The principle of relativity demands that the time shall be treated on the same footing as the other variables, and so it must therefore be a q-number On the classical theory it is known that one may solve the problem by considering the time t to be an extra co-ordinate of the system, with minus the energy (or perhaps a slightly different quantity) W as conjugate momentum In the solution of the problem there will now be complete symmetry between the new pair of variables t and $-$W and the original u pairs, except for the fact that when one performs the contact transformation to the uniformising variables, the co-ordinate t itself must be one of the new variables A P B is now defined by

$$[x, y] = \Sigma_r \left(\frac{\partial x}{\partial q_r}\frac{\partial y}{\partial p_r} - \frac{\partial x}{\partial p_r}\frac{\partial y}{\partial q_r}\right) - \frac{\partial x}{\partial t}\frac{\partial y}{\partial \mathrm{W}} + \frac{\partial x}{\partial \mathrm{W}}\frac{\partial y}{\partial t}, \tag{3}$$

and is invariant under any contact transformation of the $(2u + 2)$ variables A dynamical system is now determined by an *equation* between the $(2u + 2)$ variables instead of a *function* of $2u$ variables—namely, the Hamiltonian equation

$$\mathrm{H} - \mathrm{W} = 0, \tag{4}$$

and the equations of motion are

$$\left.\begin{aligned} q_r &= \frac{\partial \mathrm{H}}{\partial p_r} = \frac{\partial (\mathrm{H} - \mathrm{W})}{\partial p_r} \\ t &= 1 = \frac{\partial (\mathrm{H} - \mathrm{W})}{\partial (-\mathrm{W})} \\ p_r &= \frac{\partial \mathrm{H}}{\partial q_r} = -\frac{\partial (\mathrm{H} - \mathrm{W})}{\partial q_r} \end{aligned}\right\}, \tag{5}$$

and lastly

$$\begin{aligned} -\dot{\mathrm{W}} = -\mathrm{H} &= -\Sigma_r \left(\frac{\partial \mathrm{H}}{\partial q_r}\dot{q}_r + \frac{\partial \mathrm{H}}{\partial p_r}\dot{p}_r\right) - \frac{\partial \mathrm{H}}{\partial t} = -\frac{\partial \mathrm{H}}{\partial t} \\ &= -\frac{\partial (\mathrm{H} - \mathrm{W})}{\partial t}. \end{aligned} \tag{5A}$$

From these equations of motion, if x is any function of the $(2u + 2)$ variables

$$\dot{x} = \Sigma_r \left(\frac{\partial x}{\partial q_r}\,\dot{q}_r + \frac{\partial x}{\partial p_r}\,\dot{p}_r\right) + \frac{\partial x}{\partial t} + \frac{\partial x}{\partial \mathrm{W}}\,\mathrm{W}$$

$$= \Sigma_r \left(\frac{\partial x}{\partial q_r}\,\frac{\partial\,(\mathrm{H} - \mathrm{W})}{\partial p_r} - \frac{\partial x}{\partial p_r}\,\frac{\partial\,(\mathrm{H} - \mathrm{W})}{\partial q_r}\right) - \frac{\partial x}{\partial t}\,\frac{\partial\,(\mathrm{H} - \mathrm{W})}{\partial \mathrm{W}} + \frac{\partial x}{\partial \mathrm{W}}\,\frac{\partial\,(\mathrm{H} - \mathrm{W})}{\partial t}$$

or

$$\dot{x} = [x, \mathrm{H} - \mathrm{W}] \tag{6}$$

from (3)

We can take these results directly over into the quantum theory We assume that t and $-\mathrm{W}$ are a new pair of conjugate variables, and therefore satisfy the equations, supplementary to (1),

$$\left.\begin{array}{cc} tq_r - q_rt = 0, & tp_r - p_rt = 0 \\ \mathrm{W}q_r - q_r\mathrm{W} = 0, & \mathrm{W}p_r - p_r\mathrm{W} = 0 \\ \multicolumn{2}{c}{t\mathrm{W} - \mathrm{W}t = -ih} \end{array}\right\}, \tag{7}$$

and that the quantum P B $[x, y]$, defined by (2), is now the analogue of the classical expression on the right-hand side of (3). The equations of motion are assumed to be still given by (6)

The fact that a dynamical system is now specified by a Hamiltonian equation $\mathrm{H} - \mathrm{W} = 0$ instead of by a Hamiltonian function H here leads to a difficulty, since the Hamiltonian equation is not consistent with the quantum conditions (1) and (7) For example, if x is a function of the p's and q's only,

$$x\mathrm{W} - \mathrm{W}x = 0,$$

while in general

$$x\mathrm{H} - \mathrm{H}x \neq 0,$$

and these two equations are not consistent with $\mathrm{W} = \mathrm{H}$ An ordinary quantum equation gives a correct result when one equates the P B. of either side with an arbitrary quantity, and must therefore correspond to an identity on the classical theory, *i e*, a relation that remains true on being differentiated partially with respect to any of the canonical variables Now the Hamiltonian equation on the classical theory is not an identity One can perform algebraic operations upon it, but one must not differentiate it. There must be a corresponding restriction on the use of the quantum Hamiltonian equation, although it cannot easily be specified, as there is no hard-and-fast distinction between algebraic operations and differentiations on the quantum theory This uncertainty does not give any trouble in the present paper, however, as we shall follow the classical theory so closely that it will be immediately obvious whether any quantum operation corresponds to a legitimate classical operation or not

The rules for the solution of the problem on the quantum theory are now, as on the classical theory, that one must determine a set of $(2u + 2)$ uniformising variables J_0 . J_u, W_0 . W_u, say, that satisfy the following conditions :—

(i) They must be canonical variables, it being possible to verify this without the use of the Hamiltonian equation

(ii) One of the w's, w_0 say, must be just t.

(iii) The Hamiltonian equation must become a relation between the J's only

(iv) The original variables, when expressed in terms of the new variables, must be multiply periodic functions of as many of the w's as possible with the periods 2π They cannot, of course, be periodic functions of w_0, since $t = w_0$

The frequencies associated with the various transitions of the system and the corresponding intensities may now be determined as for systems for which the Hamiltonian does not contain the time explicitly

The fact that $w_0 = t$ provides us with certain information concerning the form of the transformation to the uniformising variables, as on the classical theory Since each of the uniformising variables except J_0 commutes with w_0, i e , with t, when expressed in terms of the original variables, it must be independent of W Further, since

$$[t, J_0] = [w_0, J_0] = 1 = -[t, W],$$

$J_0 + W$ commutes with t, and hence J_0, when expressed in terms of the original variables, must equal minus W plus a quantity independent of W The Hamiltonian equation $H - W = 0$ thus takes the form $H_0 + J_0 = 0$, where H_0 is a function of J_1 J_u only In consequence of these results and the fact that t commutes with each of the p's and q's, Born, Heisenberg, and Jordan's perturbation theory for systems for which the Hamiltonian contains the time explicitly,* in which t is treated as a c-number, can be justified

It should be observed that if the Hamiltonian equation of a system is $F(p_r, q_r, W, t) = 0$, it must be put in the standard form (4) before one can insert its left-hand side in the P B in the equation of motion (6) If one does not do this, but simply takes for the right-hand side of (6) the P B $[x, F]$, on the classical theory, the left-hand side would not be $\dot{x}$ but dx/dv, where v might be any variable Also, with regard to condition (iii) for the uniformising variables, the quantity $H - W$ becomes just the quantity $H_0 + J_0$, but the quantity F may not become a function of the J's only, as one may have to divide the equation $F = 0$ by a factor which is a function of the w's as well as the J's in order to make its left-hand side a function of the J's only

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* Born, Heisenberg, and Jordan, *loc. cit*, Kap. 1, § 5.

§ 3 *Quantum Mechanics of Moving Systems*

A dynamical system that is moving as a whole may be described with, for canonical variables, the Cartesian co-ordinates of the centre of gravity x_1, x_2, x_3, with p_1, p_2, p_3, the components of total momentum, for conjugate variables, together with the necessary internal variables, which are independent of the position and velocity of the centre of gravity If t is the time and W the energy, one may introduce the variables

$$x_4 = \iota ct, \qquad p_4 = \iota W/c, \tag{8}$$

where ι is a root of -1 independent of the root of -1 occurring in the quantum conditions, and c is the velocity of light, which is, of course, a c-number The principle of relativity requires complete symmetry between the x_4, p_4 and the x_1, p_1, the x_2, p_2, and the x_3, p_3 Hence, on account of the relations

$$[x_1, p_1] = [x_2, p_2] = [x_3, p_3] = 1,$$

we must have

$$[x_4, p_4] = 1$$

which gives

$$[\iota ct, \iota W/c] = 1$$

or

$$[t, W] = -1$$

The principle of relativity thus shows that $-$ W is the momentum conjugate to t, in agreement with the results of the preceding § The remaining ones of the quantum conditions (7) may be likewise obtained

Let m be the rest mass of the system, so that mc^2 is its proper energy Then m and mc^2 are functions of the internal variables only, or, when the system consists of a single particle only, so that there are no internal variables, they are c-numbers We have

$$W^2/c^2 - p_1{}^2 - p_2{}^2 - p_3{}^2 = m^2c^2 \tag{9}$$

which is the Hamiltonian equation for the system The variables p_1, p_2, p_3, W and x_1, x_2, x_3, t may be taken to be uniformising variables, as they satisfy all the conditions for this except the multiply periodic conditions for the x's, which they obviously cannot be expected to satisfy The remaining uniformising variables will be functions of the internal variables only.

The theory may be extended to systems acted upon by external fields of force, provided the classical equations of motion can be put in the Hamiltonian form. Suppose, for instance, that the system possesses a total charge e (a c-number), considered to be concentrated at its centre of gravity, and is in an electromagnetic field describable by the vector potential κ_1, κ_2, κ_3 and the scalar potential ϕ, these four quantities being given functions of x_1, x_2, x_3 and t. Instead of ϕ we may use the quantity

$$\kappa_4 = i\phi,$$

analogous to the x_4 and p_4 introduced by equation (8), so that κ_1, κ_2, κ_3, κ_4 are the components of a 4 vector. On the classical theory the equations of motion of the centre of gravity of the system may be written, if one uses the summation convention of the tensor calculus,

$$\frac{d}{ds}\left(m\,\frac{dx_\mu}{ds}\right) = \frac{e}{c}\left(\frac{\partial\kappa_\nu}{\partial x_\mu} - \frac{\partial\kappa_\mu}{\partial x_\nu}\right)\frac{dx_\nu}{ds} \qquad (\mu, \nu = 1 \quad 4)$$

$$= \frac{e}{c}\,\frac{\partial\kappa_\nu}{\partial x_\mu}\,\frac{dx_\nu}{ds} - \frac{e}{c}\,\frac{d\kappa_\mu}{ds}, \tag{10}$$

where s is the proper time defined by

$$ds^2 = c^2\,dx_\mu\,dx_\mu$$

Now define p_μ by

$$p_\mu = m\,\frac{dx_\mu}{ds} + \frac{e}{c}\,\kappa_\mu \qquad (\mu = 1 \quad 4), \tag{11}$$

instead of simply by $m\,dx_\mu/ds$, which was its previous meaning. The equations of motion (10) become

$$\frac{dp_\mu}{ds} = \frac{c}{mc}\,\frac{\partial\kappa_\nu}{\partial x_\mu}\left(p_\nu - \frac{e}{c}\,\kappa_\nu\right) \tag{12}$$

The Hamiltonian equation (9) now becomes, owing to the changed meaning of the p's

$$-\left(p_\nu \quad \frac{e}{c}\,\kappa_\nu\right)\left(p_\nu - \frac{e}{c}\,\kappa_\nu\right) - m^2c^2 \tag{13}$$

or

$$\mathrm{F} = 0$$

where

$$\mathrm{F} = \frac{1}{2m}\left(p_\nu - \frac{e}{c}\,\kappa_\nu\right)\left(p_\nu - \frac{e}{c}\,\kappa_\nu\right) + \tfrac{1}{2}mc^2,$$

while the equations (11) and (12) may be written

$$\frac{dx_\nu}{ds} = \frac{\partial\mathrm{F}}{\partial p_\nu}$$

and

$$\frac{dp_\mu}{ds} = -\frac{\partial\mathrm{F}}{\partial x_\mu}$$

Further, we have

$$\frac{\partial\mathrm{F}}{\partial m} = -\frac{1}{2m^2}\left(p_\nu - \frac{e}{c}\,\kappa_\nu\right)\left(p_\nu - \frac{e}{c}\,\kappa_\nu\right) + \tfrac{1}{2}c^2 = c^2$$

with the help of the equation $F = 0$, so that if q_r, p_r are a pair of canonically conjugate internal variables, the equations of internal motion are

$$\frac{dq_r}{ds} = \frac{\partial mc^2}{\partial p_r} = \frac{\partial m}{\partial p_r} c^2 = \frac{\partial m}{\partial p_r} \frac{\partial F}{\partial m} = \frac{\partial F}{\partial p_r}$$

$$\frac{dp_r}{ds} = - \frac{\partial mc^2}{\partial q_r} = - \frac{\partial m}{\partial q_r} c^2 = - \frac{\partial m}{\partial q_r} \frac{\partial F}{\partial m} = - \frac{\partial F}{\partial q_r}$$

All the equations of motion are thus of the Hamiltonian form (5) with the Hamiltonian function F The fact that the total differentiations are performed with respect to s instead of t is due to the Hamiltonian equation $F = 0$ not being in the standard form (4)

It is thus established that the classical equations of motion take the canonical form when the variables conjugate to the x_μ are defined by (11) * On the quantum theory we must therefore still use this definition of p_μ, and can then proceed according to rule with the Hamiltonian equation (13)

The κ's on the classical theory must satisfy the conditions

$$\frac{\partial \kappa_\mu}{\partial x_\mu} = 0, \qquad \frac{\partial^2 \kappa_\mu}{\partial x_\nu \partial x_\nu} = 0$$

These equations may be written

$$[\kappa_\mu, p_\mu] = 0, \qquad [[\kappa_\mu, p_\nu], p_\nu] = 0, \tag{14}$$

and can then be taken over into the quantum theory With the help of the first of these relations, the Hamiltonian equation (13) may be put in the forms

$$-m^2c^2 = p_\nu p_\nu - 2\frac{e}{c} p_\nu \kappa_\nu + \frac{e^2}{c^2} \kappa_\nu \kappa_\nu = p_\nu p_\nu - 2\frac{e}{c} \kappa_\nu p_\nu + \frac{e^2}{c^2} \kappa_\nu \kappa_\nu \tag{15}$$

§ 4 *Relativity Quantum Mechanics*

If we proceed to apply the method of § 2 to the systems considered in § 3, the requirements of the restricted principle of relativity will still not be completely satisfied, owing to the singular part played by the time t as a uniformising variable To get over this difficulty we must again refer to the classical theory.

The ordinary classical theorems connecting the intensities in various directions of components of the emitted radiation with the corresponding amplitudes in the Fourier expansion of the total polarisation are valid only, if the distances moved through by the electrons during a period of the component of radiation considered are small compared with the wave length of this component, i e , if the velocities of the electrons are small compared with that of light. When this condition is not satisfied, in order to determine the intensities for a given direction, say, that of the x_1 axis, one must obtain the Fourier expansion of the total polarisation in the form

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* It has been shown by W Wilson that the momenta defined in this way must be used in the ordinary quantum conditions $\int p\,dq = nh$ ['Roy Soc. Proc ,' A, vol 102, p 478 (1922)].

$$\tfrac{1}{2}\Sigma_\alpha C_\alpha \exp \{i(\alpha\omega)(t - x_1/c)\} \tag{16}$$

where the $(\alpha\omega)$'s are constants, and are the frequencies (multiplied by 2π) of the radiation emitted in this direction, and must use these amplitudes C_α instead of the usual ones. This is readily seen to be so from the fact that the interchange of energy between the system and a field of radiation moving in the direction of the x_1 axis of frequency $(\alpha\omega)$, is governed entirely by the corresponding coefficient C_α defined by (16). The x_1 in the expression (16) refers to the point at which the charge is supposed to be concentrated. If there are several charges contributing to the total polarisation, the Fourier expansion (16) of each must be obtained separately with its respective x_1, and their corresponding amplitudes can then be added. In this case one can approximate, if the relative displacements of the charges are small, by taking the x_1 of (16) to be the x_1 of the centre of gravity of the system.

Further, if the total polarisation contains a part that increases uniformly in addition to a periodically varying part, which will occur when the whole system is charged and is moving uniformly, the non periodic term to be added to (16) must be of the form, a constant times $(t - x_1/c)$, instead of a constant times t as in the elementary theory, in order that its contribution to the exchange of energy with the radiation field previously considered may vanish. The approximation of taking x_1 to refer to the centre of gravity of the system is not in general valid for this non-periodic term unless the velocity of the centre of gravity is small, and the theory would then reduce to the ordinary theory.

It should be noted that the amplitudes C_α determine directly the rate per unit area (I_1, say) at which energy of the radiation passes a fixed point at a distance r (a c-number) from the emitting system in the direction of the x_1 axis, by means of the formula

$$I_1 = \frac{e^2(\alpha\omega)^4}{8\pi c^3 r^2} |C_\alpha|^2, \tag{17}$$

and determine the rate of emission of energy by the system in the x_1 direction only through formulæ involving the velocity of the centre of gravity of the system, which will be found later to be ambiguous on the quantum theory. The distinction is important because the intensity I_1 is an observable quantity, while the rate of emission of energy by the system is not.

To express the theory of this § in terms of canonical variables, we observe that the only essential modification in the previous theory required is that our standard of a "uniformly increasing variable" must be changed from t to $(t - x_1/c)$. This can be effected, on both the classical and quantum theories, simply by taking $(t - x_1/c)$ to be a uniformising variable instead of t in the second of the conditions to be satisfied by the uniformising variables (§ 2). Of course this can be done only when one knows what to take for x_1, and at present the only cases in which the x_1 of expression (16) has a definite meaning are those when there is only one charged particle, and when one is able to take the x_1 of the centre of gravity as a sufficient approximation. The method of procedure in the general case is not yet known. The frequencies given by the theory with $(t - x_1/c)$ for a uniformising variable are the $(\alpha\omega)$'s of expression (16), which are the wave frequencies and not the frequencies of vibration of the system.

An example of the first of these cases in which x_1 has a definite meaning will be given in the next §, and an example of the second will now be considered. Take the system considered in the previous § in the absence of an external field, when the Hamiltonian equation is (9), and apply the canonical transformation

$$\left.\begin{array}{ll} t' = t - x_1/c & -\mathrm{W}' = -\mathrm{W} \\ x_1' = x_1 & p_1' = p_1 - \mathrm{W}/c \end{array}\right\} \tag{18}$$

The Hamiltonian equation becomes

$$-2p_1'\mathrm{W}'/c - p_1'^2 - p_2^2 - p_3^2 = m^2c^2$$

If we wish to consider the radiation emitted in the direction of the x_1 axis, we must take t' to be a uniformising variable, and may take for the other uniformising variables $-\mathrm{W}'$, conjugate to t', and p_1', x_1', p_2, x_2 and p_3, x_3, together with certain J's and w's that are functions of the internal variables only.

Now consider a particular component of the emitted radiation, say that corresponding to e^{iw}. We know that w commutes with p_2, p_3 and p_1', so that

$$p_2e^{iw} = e^{iw}p_2, \qquad p_3e^{iw} = e^{iw}p_3$$
$$(p_1 - \mathrm{W}/c)\,e^{iw} = e^{iw}\,(p_1 - \mathrm{W}/c)$$

Hence, according to the principles of § 1, the particular c-number values possessed by p_2, p_3 and $p_1 - \mathrm{W}/c$ before the transition are equal to those they possess after the transition, so that p_2 and p_3 are unchanged by the transition, while the change in p_1 equals $1/c$ times the change in the energy W. Hence, according to the present theory, the system experiences a recoil when it emits radiation, in agreement with the light-quantum theory. Each component of the emitted radiation is associated with two momenta of the whole system as well as with two energies

§ 5. *Theory of Compton Scattering*

Consider a free electron subjected to plane polarised monochromatic incident radiation The electron and incident radiation together may be considered to form a dynamical system whose emission spectrum can be determined by the methods of the preceding §§, although it is usually called not an emission spectrum but a scattered radiation

Suppose the incident radiation to be moving in the direction of the x_1 axis with its electric vector in the direction of the x_2 axis The electromagnetic field may then be described by the potentials

$$\kappa_1 = \kappa_3 = \kappa_4 = 0, \qquad \kappa_2 = a \cos \nu (ct - x_1) \tag{19}$$

where ν is 2π times the wave number of the incident radiation, and a determines the intensity of the incident radiation I_0 through the formula

$$I_0 = c\, a^2 \nu^2 / 8\pi \tag{20}$$

Since ν and I_0 can be measured physically they are c-numbers, and therefore so also is a We shall suppose a to be small, and shall neglect second order effects The Hamiltonian equation is, if one puts $-e$ for e in (13) and uses the values for the κ's given by (19),

$$m^2c^2 = W^2/c^2 - p_1^2 - \{p_2 + a' \cos \nu (ct - x_1)\}^2 - p_3^2 \tag{21}$$

where

$$a' = ea/c \tag{22}$$

and is a c-number Since there are no internal co-ordinates, m is now a c number, being the rest-mass of an electron

We shall determine the frequency and intensity of the radiation emitted in the direction defined by the direction cosines l_1, l_2, l_3 (c numbers) This requires that $t' = t - (l_1x_1 + l_2x_2 + l_3x_3)/c$ shall be a uniformising variable Apply the linear canonical transformation

$$\left.\begin{aligned} x_1' &= ct - x_1 & p_1 &= -p_1' + l_1 W'/c \\ x_2' &= x_2 & p_2 &= p_2' + l_2 W'/c \\ x_3' &= x_3 & p_3 &= p_3' + l_3 W'/c \\ t' &= t - (l_1x_1 + l_2x_2 + l_3x_3)/c & -W &= -W' + cp_1' \end{aligned}\right\} \tag{23}$$

which gives

$$\left.\begin{aligned}(1-l_1)\,p_1' &= -p_1 + l_1 W/c\\ (1-l_1)\,p_2' &= l_2 p_1 + (1-l_1)\,p_2 - l_2 W/c\\ (1-l_1)\,p_3' &= l_3 p_1 + (1-l_1)\,p_3 - l_3 W/c\\ (1-l_1)\,W' &= W - cp_1\end{aligned}\right\}\text{[*]} \tag{24}$$

The Hamiltonian equation (21) becomes, if one neglects a^2,

$$\begin{aligned}m^2c^2 = (-W' + cp_1')^2/c^2 &- (-p_1' + l_1 W'/c)^2\\ &- (p_2' + l_2 W'/c + a'\cos\nu x_1')^2 - (p_3' + l_3 W'/c)^2\\ &= -2W'/c \quad A - B\end{aligned} \tag{25}$$

where

$$\begin{aligned}A &= (1-l_1)\,p_1' + l_2 p_2' + l_3 p_3' + l_2 a'\cos\nu x_1'\\ &= l_1 p_1 + l_2 p_2 + l_3 p_3 - W/c + l_2 a'\cos\nu x_1'\end{aligned}$$

and

$$B = p_2'^2 + p_3'^2 + 2a' p_2' \cos\nu x_1'$$

Equation (25) takes the standard form

$$H - W' = 0 \tag{26}$$

where

$$H = -\tfrac{1}{2} c\,(m^2c^2 + B)\,A^{-1}. \tag{27}$$

Since W′ commutes with A, we could equally well have written (25) in the form

$$m^2c^2 = -2AW'/c - B$$

which would have given equation (26) with

$$H = -\tfrac{1}{2} c\,A^{-1}\,(m^2c^2 + B) \tag{27'}$$

This does not agree with (27) since A does not commute with B More generally we could easily obtain the Hamiltonian

$$H = -\tfrac{1}{2} c f_1\,(m^2c^2 + B) f_2, \tag{28}$$

where f_1 and f_2 are any two functions of the single variable A such that $f_1 f_2 = A^{-1}$ We are thus led to an inconsistency, as is always liable to happen when one is dealing with the Hamiltonian equation, or any other equation that does not correspond to an identity on the classical theory

We can get over the difficulty in the present case by showing that all Hamiltonians of the type (28) give the same values for the frequency and intensity of the emitted radiation Let

$$H^* = -\tfrac{1}{2} c f_1^*\,(m^2c^2 + B) f_2^*$$

be another such Hamiltonian, *i e*, f_1^* and f_2^* are functions of the single variable

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[*] The notation α/β is used only when α and β commute, so there is no ambiguity.

A such that $f_1{}^* f_2{}^* = A^{-1}$ and put $f_1{}^* = bf_1$ so that b must be a function of the single variable A and must commute with the f s We must then have $f_2{}^* = f_2 b^{-1}$ so that H* must be connected with the H of equation (28) by the relation

$$H^* = b\,H\,b^{-1}$$

If J_r w_r are the uniformising variables when the Hamiltonian is H then it is easily seen that $J_r{}^* = bJ_r b^{-1}$ $w_r{}^* = bw_r b^{-1}$ which are connected with the J_r w_r by a contact transformation are the uniformising variables when the Hamiltonian is H* and that H* is the same function of the $J_r{}^*$ that H is of the J_r It follows that the frequencies are the same with either Hamiltonian Further if X is any function of the variables of the system then $b\,X\,b^{-1}$ must be the same function of the $J_r{}^*$ $w_r{}^*$ that X is of the J_r w_r Now take X to be the polarisation in any direction perpendicular to the direction of emission (these being the only components of the polarisation that matter) so that

$$X = \lambda_1 x_1 + \lambda_2 x_2 + \lambda_3 x_3$$

where the λ s are c numbers satisfying $\lambda_1 l_1 + \lambda_2 l_2 + \lambda_3 l_3 = 0$ We find

$$[A\ X] = \lambda_1 l_1 + \lambda_2 l_2 + \lambda_3 l_3 = 0$$

so that X commutes with A and therefore with b We now have that X is the same function of the $J_r{}^*$ $w_r{}^*$ as it is of the J_r w_r and hence its Fourier amplitudes are the same for either Hamiltonian

Having thus established that all Hamiltonians of the type (28) lead to the same results we may proceed using the Hamiltonian (27) which is the most convenient one We see at once that p_2 and p_3 commute with H and they are therefore constants The action and angle variables are easily verified to be*

$$\begin{aligned} J &= \frac{1}{\nu(1-l_1)}\{(1-l_1)p_1 + l_2 p_2 + l_3 p_3 + l_2 a \cos \nu x_1\} \\ &\qquad\qquad \times \frac{m^2c^2 + p_2{}^2 + p_3{}^2}{m^2c^2 + p_2{}^2 + p_3{}^2 + 2a\,p_2 \cos \nu x_1} \\ &= \frac{1}{\nu(1-l_1)}\,A\,\frac{m^2c^2 + B_0}{m^2c^2 + B} \end{aligned} \tag{29}$$

where

$$B_0 = p_2{}^2 + p_3{}^2$$

and

$$w = \nu x_1 + \frac{2a\,p_2 \sin \nu x_1}{m^2c^2 + B_0}, \tag{30}$$

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* *Loc cit*, p 417

since we then have

$$[w, \mathrm{J}] = \frac{1}{\nu(1-l_1)}[w, \mathrm{A}]\frac{m^2c^2+\mathrm{B}_0}{m^2c^2+\mathrm{B}}$$
$$= \frac{1}{\nu}\left\{\nu + \frac{2a'p_2'[\sin \nu x_1', p_1']}{m^2c^2+\mathrm{B}_0}\right\}\frac{m^2c^2+\mathrm{B}_0}{m^2c^2+\mathrm{B}} = 1,$$

as

$$[\sin \nu x_1', p_1'] = \nu \cos \nu x_1'.$$

From (27) and (29) we have

$$\mathrm{H} = -\tfrac{1}{2}c\frac{m^2c^2+p_2'^2+p_3'^2}{\nu(1-l_1)\mathrm{J}}. \tag{31}$$

Since p_2' and p_3' commute with J and w, we may take them to be uniformising variables, as we then have H a function of p_2', p_3' and J only. We do not require to determine the uniformising variables conjugate to p_2' and p_3'.

There is only one component of radiation emitted, namely, that corresponding to e^{iw}. Since p_2' and p_3' commute with e^{iw}, it follows from § 1 that their c-number values remain unchanged during a transition, while the value of J is reduced by h. Thus, if we use the symbol Δ to denote the increase in the c-number value of any constant of integration during a transition, we have

$$\Delta p_2' = 0, \quad \Delta p_3' = 0, \quad \Delta \mathrm{J} = -h,$$

while if ν' is 2π times the wave number of the emitted radiation, we have from Bohr's frequency condition

$$\Delta\mathrm{H} = -ch\nu' = \Delta\mathrm{W}'$$

If we neglect small quantities proportional to a or a', the equation $\Delta\mathrm{J} = -h$ gives, from (29),

$$\Delta\mathrm{A} = -h\nu(1-l_1)$$

or

$$\Delta p_1' = -h\nu$$

We now find, using the transformation equations (23),

$$\left.\begin{aligned} \Delta p_1 &= h\nu - l_1 h\nu' \\ \Delta p_2 &= -l_2 h\nu' \\ \Delta p_3 &= -l_3 h\nu' \\ \Delta\mathrm{W}/c &= h\nu - h\nu' \end{aligned}\right\} \tag{32}$$

If one neglects a, then p_1, p_2, p_3 and W are the ordinary momenta and kinetic energy of the electron, and equations (32) are then the equations that express the conservation of momentum and energy on Compton's light-quantum theory of scattering[*] The present theory thus gives the same values for the frequency of the scattered radiation and the recoil momentum of the electron as the light-quantum theory

§ 6 *Intensity of the Scattered Radiation*

To obtain the intensity of the emitted radiation, we must determine the amplitudes of vibration in two mutually perpendicular directions that are both perpendicular to the direction of emission (l_1, l_2, l_3) We may take the direction cosines of these two directions to be

$$l_3, \quad -\frac{l_2 l_3}{1-l_1}, \quad \frac{l_2^2}{1-l_1} - l_1 \quad \text{and} \quad l_2, \quad \frac{l_3^2}{1-l_1} - l_1, \quad -\frac{l_2 l_3}{1-l_1},$$

which are easily verified to satisfy all the necessary conditions, and put

$$\left.\begin{aligned} \mathrm{X} &= l_3 x_1 - \frac{l_2 l_3}{1-l_1} x_2 + \left(\frac{l_2^2}{1-l_1} - l_1\right) x_3 \\ \mathrm{Y} &= l_2 x_1 + \left(\frac{l_3^2}{1-l_1} - l_1\right) x_2 - \frac{l_2 l_3}{1-l_1} x_3 \end{aligned}\right\} \tag{33}$$

We have from (27)

$$\begin{aligned} [x_1', \mathrm{H}] &= \tfrac{1}{2}c\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-1}[x_1', \mathrm{A}]\,\mathrm{A}^{-1} = \tfrac{1}{2}c\,(1-l_1)\,(m^2c^2 + \mathrm{B})\ \mathrm{A}^{-2} \\ [\sin \nu x_1', \mathrm{H}] &= \tfrac{1}{2}c\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-1}[\sin\ \nu x_1', \mathrm{A}]\,\mathrm{A}^{-1} \\ &= \tfrac{1}{2}c\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-1}\nu\,(1 - l_1)\cos\ \nu x_1' \,.\, \mathrm{A}^{-1} \\ &= -\nu(1 - l_1)\ \mathrm{H}\cos\ \nu x_1'\ \ \mathrm{A}^{-1} \\ [x_3', \mathrm{H}] &= -\tfrac{1}{2}c\,[x_3', \mathrm{B}]\,\mathrm{A}^{-1} + \tfrac{1}{2}c\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-1}[x_3', \mathrm{A}]\,\mathrm{A}^{-1} \\ &= -\tfrac{1}{2}c\ \ 2p_3'\mathrm{A}^{-1} + \tfrac{1}{2}cl_3\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-2} \\ &= \tfrac{1}{2}c\,(l_3 + cp_3'/\mathrm{H})\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-2} \\ &= (l_3 + cp_3'/\mathrm{H})/(1-l_1)\ \ [x_1'\ \mathrm{H}] \end{aligned}$$

so that

$$[(1-l_1)\,x_3' - (l_3 + cp_3'/\mathrm{H})\,x_1', \mathrm{H}] = 0,$$

or

$$(1-l_1)\,x_3' - (l_3 + cp_3'/\mathrm{H})\,x_1' = \text{const} \tag{34}$$

Also

$$\begin{aligned} [x_2', \mathrm{H}] &= -\tfrac{1}{2}c\,[x_2', \mathrm{B}]\,\mathrm{A}^{-1} + \tfrac{1}{2}c\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-1}[x_2', \mathrm{A}]\,\mathrm{A}^{-1} \\ &= -\tfrac{1}{2}c\,(2p_2' + 2a'\cos\ \nu x_1')\,\mathrm{A}^{-1} + \tfrac{1}{2}cl_2\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-2} \\ &= -a'c\cos\nu x_1'\ \ \mathrm{A}^{-1} + \tfrac{1}{2}c\,(l_2 + cp_2'/\mathrm{H})\,(m^2c^2 + \mathrm{B})\,\mathrm{A}^{-2} \\ &= a'c/\nu\,(1-l_1)\,\mathrm{H}\ \ [\sin\ \nu x_1', \mathrm{H}] + (l_2 + cp_2'/\mathrm{H})/(1-l_1)\ \ [x_1', \mathrm{H}], \end{aligned}$$

so that

$$(1-l_1)x_2' - a'c/\nu\mathrm{H}\ \ \sin\ \nu x_1' - (l_2 + cp_2'/\mathrm{H})\,x_1' = \text{const} \tag{35}$$

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[*] Compton, 'Phys. Rev.,' vol. 21, p. 483 (1923)

From equations (23) we find

$$x_2 = x_2', \quad x_3 = x_3', \quad (1-l_1)\,x_1 = ct' - x_1' + l_2x_2' + l_3x_3',$$

so that the first of equations (33) may be written

$$\begin{aligned}(1-l_1)\,\mathrm{X} &= l_3\,(ct' - x_1' + l_2x_2' + l_3x_3') - l_2l_3x_2' + (l_2^2 - l_1 + l_1^2)\,x_3' \\ &= l_3ct' - l_3x_1' + (1-l_1)x_3' \\ &= l_3ct' + cp_3'/\mathrm{H} \cdot x_1' + \text{const}\end{aligned}$$

with the help of (34), and similarly the second of equations (33) may be written

$$\begin{aligned}(1-l_1)\,\mathrm{Y} &= l_2\,(ct' - x_1' + l_2x_2' + l_3x_3') + (l_3^2 - l_1 + l_1^2)\,x_2' - l_2l_3x_3' \\ &= l_2ct' - l_2x_1' + (1-l_1)\,x_2' \\ &= l_2ct' + cp_2'/\mathrm{H} \cdot x_1' + a'c/\nu\mathrm{H} \cdot \sin \nu x_1' + \text{const}\end{aligned}$$

with the help of (35)

We are interested only in the periodic parts of X and Y, and may omit the constant parts and the parts that increase uniformly with respect to t' or w To the first order in a equation (30) for w may be written

$$\nu x_1' = w - 2a'p_2'/(m^2c^2 + \mathrm{B}_0) \cdot \sin w,$$

and we now find for the periodic parts of x and y, with the help of (31),

$$\left.\begin{aligned}\mathrm{X} &= -\frac{cp_3'}{(1-l_1)\,\mathrm{H}}\,\frac{2a'p_2'}{\nu\,(m^2c^2+\mathrm{B}_0)}\sin w = \frac{4a'p_2'p_3'\mathrm{J}}{(m^2c^2+\mathrm{B}_0)^2}\sin w \\ \mathrm{Y} &= \left\{-\frac{cp_2'}{(1-l_1)\,\mathrm{H}}\,\frac{2a'p_2'}{\nu\,(m^2c^2+\mathrm{B}_0)} + \frac{a'c}{(1-l_1)\,\nu\mathrm{H}}\right\}\sin w \\ &= -\frac{2a'(m^2c^2 - p_2'^2 + p_3'^2)\,\mathrm{J}}{(m^2c^2+\mathrm{B}_0)^2}\sin w\end{aligned}\right\} \quad (36)$$

These equations may be written

$$\mathrm{X} = -2ia'\left\{\frac{p_2'p_3'\mathrm{J}}{(m^2c^2+\mathrm{B}_0)^2}\,e^{iw} - e^{-iw}\,\frac{p_2'p_3'(\mathrm{J}-h)}{(m^2c^2+\mathrm{B}_0)^2}\right\}$$

$$\mathrm{Y} = ia'\left\{\frac{(m^2c^2 - p_2'^2 + p_3'^2)\,\mathrm{J}}{(m^2c^2+\mathrm{B}_0)^2}\,e^{iw} - e^{-iw}\,\frac{(m^2c^2 - p_2'^2 + p_3'^2)\,(\mathrm{J}-h)}{(m^2c^2+\mathrm{B}_0)^2}\right\}$$

The coefficients in front of e^{iw} and behind e^{-iw} in the expansion of X or Y are not conjugate imaginaries, owing to the fact that J and w are not real All the same, their product must still be a quarter of the square of the amplitude of vibration, expressed as a function of the initial value of the action variable We thus obtain for the sum of the squares of the amplitudes of X and Y the value

$$\begin{aligned}\mathrm{C}^2 &= 4\,a'^2\,\{4\,p_2'^2p_3'^2 + (m^2c^2 - p_2'^2 + p_3'^2)^2\}\,\mathrm{J}\,(\mathrm{J}-h)/(m^2c^2+\mathrm{B}_0)^4 \\ &= \frac{4a'^2\,\mathrm{J}\,(\mathrm{J}-h)}{(m^2c^2 + p_2'^2 + p_3'^2)^2}\left\{1 - \frac{4m^2c^2p_2'^2}{(m^2c^2 + p_2'^2 + p_3'^2)^2}\right\}. \end{aligned} \qquad (37)$$

If the electron is initially at rest, except for the small oscillations caused by the incident radiation, we must substitute for p_2', p_3' and J their values determined by the relations

$$p_1 = p_2 = p_3 = 0, \qquad W = mc^2$$

which give, from (24)

$$p_1' = l_1 mc/(1 - l_1) \qquad p_2' = - l_2 mc/(1 - l_1) \qquad p_3' = - l_3 mc/(1 - l_1)$$

$$m^2c^2 + B_0 = m^2c^3 + p_2'^2 + p_3'^2 = 2m^2c^2/(1 - l_1)$$

and

$$J = A/\nu(1 - l_1) = - mc/\nu(1 - l_1)$$

with neglect of a The value of C^2 given by (37) now reduces to

$$C^2 = \frac{a'^2}{m^2c^2\nu^2}(1 - l_2^2)\left(1 + \frac{h\nu(1 - l_1)}{mc}\right) = \frac{a'^2}{m^2c^2\nu^2}(1 - l_2^2)\frac{\nu}{\nu'}$$

if we use the Compton relation connecting ν' with ν, namely,

$$\frac{1}{\nu'} = \frac{1}{\nu} + \frac{h(1 - l_1)}{mc}$$

The intensity of the emitted radiation at a distance r from the emitting electron is now given by equation (17) with $c\nu'$ substituted for $(\alpha\omega)$, i e ,

$$I = \frac{e^2c^4\nu'^4}{8\pi c^3r^2}\frac{a'^2}{m^2c^2\nu^2}\frac{\nu}{\nu'}(1 - l_2^2) = \frac{e^4 I_0}{m^2c^4r^2}\frac{\nu'^3}{\nu^3}(1 - l_2^2) \tag{38}$$

with the help of (20) and (22) This is just $(\nu'/\nu)^3$ times its value according to the classical theory

If the incident radiation is unpolarised, one must average (38) for all directions of polarisation of the incident radiation, and the result that the actual intensity is $(\nu'/\nu)^3$ times its classical value still holds This result is not very different from Compton's formula* for the intensity of the scattered radiation In particular, they agree when the angle of scattering is 0 or 180°

§ 7 *Comparison with Experiment*

The result obtained in the preceding § that the intensity of the radiation scattered by a free electron in any direction is $(\nu'/\nu)^3$ times its value, according to the classical theory, where ν'/ν is the ratio of the wave number of the radiation scattered in that direction to the wave number of the incident radiation, admits of comparison with experiment This is the first physical result obtained from the new mechanics that had not been previously known †

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* Compton, *loc. cit.*, equation (27)

† *Note added, May*, 1926 —This result for unpolarised incident radiation has recently been obtained independently by Breit from correspondence principle arguments ('Phys Rev ,' vol 27, p 362, 1926).

The quantum formula for the intensity at distance r of the radiation scattered by N electrons with plane polarised incident radiation of intensity I_0 is

$$I(\theta, \phi) = I_0 \frac{Ne^4}{r^2m^2c^4} \frac{\sin^2\phi}{\{1+\alpha(1-\cos\theta)\}^3}, \tag{39}$$

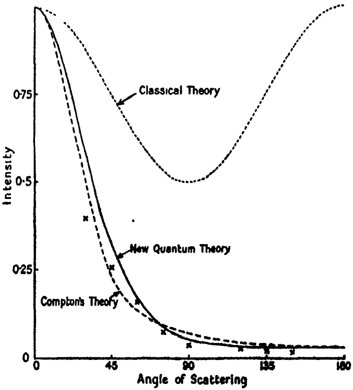
where

$$\alpha = h\nu/mc$$

and θ is the angle of scattering and ϕ the angle between the direction of the scattered radiation and the direction of the electric vector of the incident radiation For unpolarised incident radiation the formula is

$$I(\theta) = I_0 \frac{Ne^4}{2r^2m^2c^4} \frac{1+\cos^2\theta}{\{1+\alpha(1-\cos\theta)\}^3} \tag{40}$$

The full curve in the figure shows the variation of the intensity of the scattered radiation with the angle of scattering according to formula (40) for unpolarised incident radiation of wave length 0·022 A, which makes $\alpha = 1·1$ The lower



broken curve is the result given by Compton's theory,* and the upper broken curve is given by the classical theory The crosses indicate experimental values obtained by Compton, which have been taken from Compton's paper † It will be observed that the experimental values are all less than the values given by the present theory, in roughly the same ratio (75 per cent), which shows that the theory gives the correct law of variation of intensity with angle, and suggests that in absolute magnitude Compton's values are 25 per cent too small

One may easily obtain a formula for the total energy removed from the primary beam by scattering, by integrating $\mathrm{I}(\theta)\,\nu/\nu'$ over all solid angles The result is

$$\mathrm{I}_0\,\frac{2\pi\mathrm{N}e^4}{m^2c^4}\,\frac{1+\alpha}{\alpha^2}\left\{\frac{2(1+\alpha)}{1+2\alpha}-\frac{1}{\alpha}\log(1+2\alpha)\right\}$$

which for ordinary values of α lies very close to Compton's expression

$$\mathrm{I}_0\,\frac{8\pi}{3}\,\frac{\mathrm{N}e^4}{m^2c^4}\,\frac{1}{1+2\alpha},$$

(*e g*, for $\alpha = 1$ our formula gives a result 5 7 per cent greater than Compton's), and is in very good agreement with experiment

According to the present theory the state of polarisation of the scattered radiation is the same as on the classical theory, since the intensity of either polarised component of the scattered radiation in any direction is $(\nu'/\nu)^3$ times its classical value The radiation scattered through 90° is thus plane polarised for unpolarised incident radiation This result might have been expected from the correspondence principle, since it holds on the classical theory for an electron moving with either the initial velocity (*i e*, zero) or the final velocity of the quantum process It does not hold for an electron recoiling with that velocity that gives the correct frequency distribution when the electron is scattering according to the classical theory, and for this reason previous theories have predicted a shift from 90° for the angle of scattering which gives plane polarisation ‡ Experiments have been performed by Jauncey and Stauss to settle this question § They found no shift with incident radiation of 0 54 Å, and a shift of 2½°, less than half the value they expected, with incident radiation of 0 25 Å, these results are slightly in favour of the present theory which requires no shift. Great accuracy was not attainable owing to the difficulties caused by stray radiation

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* Compton, *loc cit.*, equation (27) Other formulæ have been obtained by Jauncey, 'Phys. Rev,' vol. 22, p. 233 (1923).

† Compton, *loc. cit.*, fig (7)

‡ See Jauncey, 'Phys. Rev,' vol. 23, p 313 (1924)

§ Jauncey and Stauss, 'Phys. Rev,' vol 23, p. 762 (1924)

BAKERIAN LECTURE.—*Diffuse Matter in Interstellar Space*

By A S EDDINGTON, F R S

(Received May 21, 1926)

1 The title of this lecture naturally provokes the question, Is there any appreciable quantity of matter in ordinary regions of space between the stars ? I admit that it is rather an important question, and I should scarcely feel justified in devoting a Bakerian lecture to the subject if I did not think the answer was in the affirmative But from the narrower astronomical point of view it is not a question to be insisted on at the outset Astronomers are, in fact, so placed that they must presume the existence of such matter unless or until its absence is proved For many years interstellar matter has figured in astronomical investigations, but chiefly with a *negative* importance Three examples may be given—

(1) In determining spectroscopic parallaxes and in gauging the distances of clusters and spiral nebulæ by means of Cepheid variables it is assumed that there is no absorption or scattering of light by interstellar matter

(2) Studies of stellar evolution on the hypothesis that the mass of a star diminishes at a rate corresponding to its radiation assume that there is no compensating accretion of mass by sweeping up interstellar matter

(3) Investigations of the dynamics of the stellar system are vitally affected if the controlling gravitational field is due not to the stars but to interstellar matter—distributed possibly in a way quite different from the observed distribution of the stars Moreover, in such problems it is usually assumed that there is no appreciable resisting medium

In relation to these studies a consideration of diffuse matter in space is not a speculation but a precaution The precaution must extend to a discussion of its physical properties—we must work out as far as possible the properties of a thing before we can weigh the evidence for or against its existence.

The evidence, to be considered in due course, will be found to fall mainly into two sections Firstly, we recognise in the sky certain regions—nebulæ—which undoubtedly contain diffuse matter, and theory indicates that the thinning out of matter at the edges of these is so slow that the density does not become entirely negligible in any part of the stellar system Secondly, it seems probable that the phenomenon of fixed calcium and sodium lines in certain stars is due to absorption by a diffuse cloud in space.

2. The first part of this investigation is occupied with estimates of the density, temperature and state of ionisation of the matter. As the results have been reached by a kind of successive approximation in which the final conclusions of each section involve reference to the results of other sections, we state these conclusions here :—

(1) The density at an average point in space is about 10^{-24} gm./cm.^{3}

(2) The temperature (defined by the mean molecular speed) is of the order 10,000°.

(3) The atoms are ionised down to a potential 15–20 volts, so that most valency electrons are set free but the inner groups are intact.

The second part develops the consequences which might affect astronomical observation, and includes discussions of the "fixed" lines in stellar spectra, general absorption of light in space, and accretion of mass by the stars.

PART I.—PHYSICAL CONDITION OF INTERSTELLAR MATTER.

Density of Matter in Space.

3. We derive an upper limit to the general density in space from dynamical considerations. There must be some relation between the average velocities of the stars and the gravitation potential in the stellar system. Consider, for example, a density equivalent to 10 hydrogen atoms per cu. cm. or 1·66 . 10^{-23} gm./cm.^{3} This gives a mass $128 \times \odot$ in a sphere of 5 parsecs radius. A sphere of 5 parsecs round the sun is believed to contain 30–40 lucid stars (reckoning double stars as one) and their average mass may be taken as ½ to $1 \times \odot$. Hence on this assumption the uncollected matter of the universe would amount to four or five times the mass aggregated into stars.

It is the opinion of investigators of stellar motions that the invisible matter (including dark stars, if any) cannot greatly exceed the mass of the recognised stars. Kapteyn,[*] for example, found an average mass of $1{\cdot}6 \times \odot$ per lucid star. (This refers to the total mass in space.) From a different theory of the distribution of stellar motions the writer[†] found the total density near the sun to be "not much greater than" $10 \times \odot$ in a sphere of 5 parsecs radius. The reason for these conclusions can be seen by various rough arguments. The period of orbital revolution in any sphere of uniform density 1·6 . 10^{-23} is 93 million years; a star attaining the moderate distance of 500 parsecs from the centre of gravity of the system must traverse at least 2,000 parsecs in the period, this requires an average speed of at least 21 km per sec, which is not far short of the average stellar speed Again, taking our star-cloud to correspond roughly to a uniform sphere of 1,000 parsecs radius, we find that a star would acquire a speed of 66 km per sec in falling from the boundary to the centre The above distances (500 and 1,000 parsecs) are at any rate of the order of magnitude that we must ascribe to the average stellar orbit, the actual galactic system thins out considerably in a distance of 500 parsecs towards the galactic poles, but has very much greater extension in the galactic plane Hence for a density about 10^{-23} there is general agreement between the required orbital velocities and the observed velocities of the stars, for a tenfold increase the figures would show a serious misfit, whilst a density 10^{-21} would require stellar velocities on about ten times the observed scale

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[*] 'Ap. J.,' vol. 55, p. 314.

[†] 'Monthly Notices,' vol. 75, p. 375.

It is perhaps unprofitable to define a calculation which can only be a rough estimate of order of magnitude, but one further point may be mentioned Stars of very high velocity seem to be sharply differentiated from stars of moderate velocity, inasmuch as the former move almost exclusively towards one hemisphere of the sky[*] It is reasonable to assume that these are not permanent members of our local cluster and have dropped into it from other clusters lying on one side Clearly there could be no such asymmetry in the motion of permanent members which describe orbits in the comparatively short period of 10^8 years The limit dividing the intruders from the permanent members should be the velocity of escape—$66\sqrt{3} = 115$ km per sec for the above data The observed division is at about 70 km. per sec., so that not much modification of the assumed data is required.

The dynamical method does not enable us to set a lower limit to the density of interstellar matter Although a total mass rather greater than that of the recognised stars seems to suit the stellar velocities best, we cannot say definitely that the mass of the lucid stars is insufficient Moreover, there is an unknown addition required for dark stars and recognised nebulæ Methods to be considered later suggest a density about 10^{-24}; but as it is more profitable to work with an upper limit we shall here consider a standard density of 10 hydrogen atoms per cu cm or 1 66 10^{-23}

4 To obtain an idea of the nature of this gas we calculate the order of magnitude of the free path. For average atomic weight 20 and atomic radius 10^{-8} cm. it would be 1 1 . 10^{10} km —about the diameter of the orbit of Neptune. The temperature of the interstellar gas will later be estimated at 10,000°, this gives

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[*] J H Oort, 'Bull Astr Inst. Netherlands,' No. 23.

an average atomic velocity 3 2 km per sec and a duration of free path 110 years.

But it will be shown later that the material is ionised and the free path is shortened by the electrical forces between the ions. It will be typical of the actual conditions to take the atoms (of weight 20) doubly ionised, so that there is one free electron per cu cm An encounter is taken to correspond to a deflection of 90° or more The results are—

Free path for ions * Length 10^8 km Duration 1 year

Free path for electrons Length 5 2 10^8 km Duration 10 days

An ion encounters and deflects an electron about once in 5 days

The collisions are sufficiently frequent to ensure that the material is a genuine gas with a Maxwellian distribution of velocities and not a collection of particles describing astronomical orbits The gas has a definite temperature corresponding to the average kinetic energy of its ions and electrons We use the term *temperature of material* exclusively with this meaning, and without reference to internal degrees of freedom

5 Another mode of estimating the density is based on the general extent of the condensations observed in the medium A diffuse nebula (luminous or dark) is regarded as a local condensation of the general cloud Even in these condensations the density must still be extremely low, and the argument by which we shall find a temperature of 10,000° for diffuse matter applies equally to the nebulæ—to the bright nebulæ at any rate We can therefore assume that the equilibrium of the nebulæ is isothermal and adopt a temperature of 10,000° throughout

The condensations must be more or less in equilibrium and the distribution of density should therefore conform roughly to the theory of an isothermal gas-sphere Let ρ_0 be the central density, ρ the density at distance r from the centre, and let

$$\rho = \rho_0 e^u \tag{1}$$

Then it can be shown that u satisfies the differential equation

$$\frac{d^2u}{dz^2} + \frac{2}{z}\frac{du}{dz} + e^u = 0,$$

the solution of which is tabulated by Emden (*Gaskugeln*, p 135) Here z represents r measured in a particular unit given by

$$r = \left(\frac{\mathfrak{R}\mathrm{T}}{4\pi\mathrm{G}\mu\rho_0}\right)^{\frac{1}{2}} z, \tag{2}$$

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* The result for ions is only rough, as a strict calculation is difficult.

where $\mathfrak{R} = 8.26 \cdot 10^7$, μ is the average molecular weight in terms of hydrogen and G the constant of gravitation $6.66 \cdot 10^{-8}$. Taking $\mu = 10$,* and converting r from centimetres to parsecs, this gives

$$r = (10^{20}\rho_0)^{-\frac{1}{2}} z \text{ parsecs.} \tag{3}$$

The diffuse nebulæ will (if they are not rapidly growing or dissipating) shade off indefinitely into the general interstellar distribution. We have therefore to ask ourselves the question, Taking an average point of space not disturbed by unusual proximity to any nebula, what will be the order of magnitude of its distance from the nearest nebulæ? Several diffuse nebulæ are supposed to be within about 200 parsecs from the sun, and I should judge that the answer is about 150 parsecs. (This, of course, refers to reasonably central parts of the galactic system; the density of interstellar matter will no doubt fade away at the confines of the system.)

By Emden's table giving e^u as a function of z we can find the density ρ at distance r for any assumed value of ρ_0.

Table I

r	ρ_0	r/z	z	$e^u = \rho/\rho_0$	ρ
100 parsecs	10^{-24}	100	1	0.853	$0.9 \cdot 10^{-24}$
	10^{-22}	10	10	0.0238	$2.4 \cdot 10^{-24}$
	10^{-20}	1	100	0.000175	$1.7 \cdot 10^{-24}$
	10^{-18}	0.1	1,000	0.0000020	$2.0 \cdot 10^{-24}$
200 parsecs	10^{-24}	100	2	0.571	$5.7 \cdot 10^{-25}$
	10^{-22}	10	20	0.0045	$4.5 \cdot 10^{-25}$
	10^{-20}	1	200	0.000051	$5.1 \cdot 10^{-25}$
	10^{-18}	0.1	2,000	0.00000049	$4.9 \cdot 10^{-25}$

It will be seen that the value of ρ is nearly independent of ρ_0.† Owing to this independence nebulæ of widely different central density (and correspondingly different scale of extension) could all be in approximate equilibrium with the same interstellar medium.

By interpolation the density at 150 parsecs from the nearest nebula is 10^{-24}, and we therefore adopt this as typical of any ordinary region of interstellar space.

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* *E.g.*, for Na_+, $\mu = 11.5$; for Ca_{++}, $\mu = 13.3$.

† The curious unsteadiness of the figures in the last column is not due to roughness of the calculation. Keeping r fixed and regarding ρ as a function of ρ_0, ρ has a maximum near $z = 4$, a minimum near $z = 40$, and another maximum near $z = 400$.

The law of decrease of density in the nebula itself is as follows –

$z =$	0	1	2	3	5	7	10
$\rho/\rho_0 =$	1	0·85	0·56	0·35	0·13	0·06	0·024

The semi-diameters of typical diffuse nebulæ are reckoned to be 5–10 parsecs, so that this law of fading will represent the actual extension of these nebulæ if the unit or z is about 1 parsec By (3) this gives the central density of a nebula

$$\rho_0 = 10^{-20}$$

The determination should be fairly trustworthy and it is consistent with other knowledge of the densities of nebulæ If ρ_0 were much higher the mass a nebula of 5 parsecs extension would be too great and would cause high velocities of the stars attracted by it The mass is in any case far greater than that of the stars contained in the nebulæ, this justifies our neglect of the attraction of the stars in applying the theory of the isothermal gas-sphere *

We can deduce from (3) that the masses of the diffuse nebulæ are proportional to their linear dimensions, and hence that the gravitational potential at corresponding points is the same for all

Temperature of Space

6 The total light received by us from the stars is estimated to be equivalent to about 1,000 first magnitude stars † Allowing an average correction to reduce visual magnitude of stars other than types F and G to bolometric magnitude, the heat of the stars is equivalent to about 2,000 stars of bolometric magnitude $1^m\,0$

A star of absolute bolometric magnitude 1 0 radiates 36 times as much heat as the sun or $1\ 37\ \ 10^{35}$ ergs per sec At the standard distance of 10 parsecs ($3\ 08\ \ 10^{19}$ cm) this gives a flow of $1\ 15\ \ 10^{-5}$ ergs per sq cm per sec The energy-density at this distance is obtained by dividing by the velocity of propagation, hence the energy-density due to a star of apparent bolometric magnitude $1^m\,0$ is $3\ 8\ \ 10^{-16}$ ergs/cm^3 Multiplying by 2,000, the energy-density of starlight is

$$7\ 7\ \ 10^{-13}\ \text{ergs/cm}^3$$

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* For this and other reasons the method does not apply to planetary nebulæ, in which the main mass is probably that of the central star A nebula of central density 10^{-20} contains a mass $21{,}000 \times \odot$ within 5 parsecs radius and $48{,}000 \times \odot$ within 10 parsecs radius

† See, for example, S. Chapman, 'Monthly Notices,' vol 74, p 450

The corresponding effective temperature calculated from Stepho Stefan's law is

3° 2 absolute

In a normal region of space away from the preponderating influence of any one star this constitutes the whole field of radiation, and a black body will there take up a temperature 3° 2 in order that its emission may balance the radiation falling on it and absorbed by it This is sometimes called the temperature of space, and is in fact the temperature as registered by a black-bulb thermometer If, however, our test object is not a black body but a highly diffuse gas the corresponding "temperature of space" is entirely different

It was pointed out by C Fabry* that matter with strong selective absorption can rise to much higher temperature The following table will help to fix ideas Instead of the whole density of the radiation, we calculate the density of radiation of given wave-length λ, and equate it to the density at the same wave-length of equilibrium (black body) radiation of temperature T_λ

Table II —Equivalent Temperatures of Interstellar Radiation †

λ	T_λ
600 Å	4,707°
2,000	1,750
4,000	967
6,000	690

A substance capable of absorbing and radiating only in wave-length 4,000 would rise to temperature 967°, because at this temperature it is in equilibrium with the external field of radiation so far as λ 4,000 is concerned This illustration is too abstract to be much of a practical guide ‡ In general a number of varieties of interchange of energy between radiation and matter will be occurring, each tendency to bring the matter to the temperature T_λ corresponding to the λ concerned in the process We have to discuss carefully which process will gain the upper hand in controlling the temperature of diffuse matter in space

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* 'Astrophys Jour,' vol 45, p 269

† In this calculation 5 per cent of the radiation was taken to come from stars at 18,000°, 10 per cent 12,000°, 20 per cent 9,000°, 40 per cent 6,000°, 25 per cent, 3,000°, the total density being taken at the round figure 10^{-13} ergs/cm ^{3}

‡ Conversion of energy of excitation into translatory energy can occur by radiationless processes (superelastic collisions) We have to assume that this radiationless interchange is occurring in the ideal substance, so as to rule out the objection that the temperature 967° refers only to a particular internal degree of freedom and does not correspond with the temperature as here defined

7 Energy is transferred from radiation to interstellar matter by the following processes —

(1) Ionisation of atoms (photo-electric effect)
(2) Continuous absorption during encounters of electrons with atoms (orbit switches)
(3) Excitation of atoms (line absorption)
(4) Scattering of free electrons

The four converse processes transfer energy from matter to radiation

We first show that processes (3) and (4) are negligible compared with (1) In (3) an atom absorbs a quantum of energy, holds it for about 10^{-8} sec, and then re-radiates it in one or several steps There is no transfer to kinetic energy of molecular motion and therefore no effect on the temperature of the material In denser gas this process can raise the temperature in the following way Sometimes before the 10^{-8} sec has elapsed the excited atom meets an electron and an explosive collision results, the energy of excitation being thrown into the energy of rebound But at the density under consideration the atom meets an electron only once in five days, so that only one excitation in 10^{13} can lead to further consequences, in the remainder nothing is done with the energy, which is merely handed back to the radiation field Evidently excitation cannot compete with ionisation, for in ionisation a considerable fraction of every quantum absorbed goes straight into kinetic energy of motion of electrons

A minute fraction of the energy absorbed in line-absorption passes directly into energy of thermal agitation, since an atom which is continually excited and relapsing receives a series of impulses of radiation pressure This kinetic energy is to the excitation energy in the ratio of the mass of the quantum to twice the mass of the atom, say, 10^{-10} * It is evidently inefficacious compared with ionisation, although if it were acting alone it would ultimately bring the temperature to T_λ

Process (4) is interesting because it is the only one which endeavours to establish the low black-body temperature of 3° 2 The coefficient of scattering by free electrons is the same for all wave-lengths (until we approach γ-ray wave-lengths), so that the interstellar radiation will act equivalently to equilibrium radiation of the same density and tend to set up the corresponding low

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* The momentum $h\nu/c$ of the quantum imparts to an atom of mass M a velocity $h\nu/Mc$ and kinetic energy $\frac{1}{2}M(h\nu/Mc)^2$ The ratio of this to $h\nu$ is $h\nu/c^2 : 2M$

temperature. For energy-density 10^{-12} ergs per cu. cm. the amount flowing through 1 sq. cm. in a year is 10^{6} ergs. An electron offers a scattering obstruction equal to six times its cross-section or $6{\cdot}7 \cdot 10^{-25}$ sq. cm. Thus each free electron scatters $6 \cdot 10^{-19}$ ergs or $2 \cdot 10^{-29}$ units of momentum per year. Even if the whole of this momentum were opposed to the motion of the electron it would retard it no more than a millimetre per sec. per annum. There is no cumulative effect because within the year the electron will have been captured and its place taken by a refreshed electron.

Accordingly we have only to consider the processes (1) and (2) which produce effects on an incomparably greater scale.

For those who do not wish to follow the detailed discussion of these two processes in §§ 8–11, I will give here an elementary explanation of why they lead to a very high temperature. By ionisation electrons are being shot out of the atoms in all directions with considerable speed. If nothing very important happens to them before they are recaptured they will constitute an electron gas with temperature determined by the mean energy of expulsion. Now it is well known that in the photo-electric effect the velocity of the expelled electrons depends on the *quality* and not on the *intensity* of the radiation; for a given source of light the velocity is the same whatever the distance from the source. Hence the temperature of our electron gas will be the same in the depths of space as in a region close up to a star; distance diminishes the rate of production of the electron gas but not its temperature. The heat of the electrons is continually renewed so that the atoms are ultimately warmed up to the same temperature. The high temperature of the interstellar medium is thus a typical quantum effect; the stellar radiation is extremely attenuated and its rate of activity is low, but the quantum concentration remains, so that what it does do is done with unabated vigour.

This argument is subject to reservations. If pushed to extreme length it would seem to signify that a single star could maintain the whole diffuse matter of the universe at high temperature. As the treatment is difficult, consideration of this limitation is deferred to § 14. It is perhaps the weakest part of our theory that we are not able to show more decisively that the limit is satisfied in actual interstellar conditions. It is this limit (depending ultimately on process (2)) which decides that as interstellar matter condenses it ceases to have a high temperature and tends towards the black-body temperature of space; the fall will begin at low densities long before processes (3) and (4) become significant.

8. By the process of ionisation electrons are shot out from the atoms with high velocities. Our first step is to calculate the "initial temperature" of the

expelled electrons—that is to say the temperature corresponding to the mean kinetic energy of projection.

To simplify the conditions we suppose that the stars are black bodies all of the same effective temperature T. The interstellar radiation is then *evenly diluted* equilibrium radiation, the energy density between ν and $\nu + d\nu$ being

$$\frac{C\nu^3 d\nu}{e^{h\nu/RT} - 1} \tag{1}$$

where C is a constant very much smaller than the constant in Planck's law. Suppose also that we are concerned only with one ionisation potential ν_0 (in frequency units). The ordinary law of continuous absorption for X rays is

$$k \propto \nu^{-3} \qquad (\nu > \nu_0)$$

But as a precaution in applying this to longer wave lengths we shall adopt the more general law

$$k \propto \nu^{-3-s} \qquad (\nu > \nu_0) \tag{2}$$

By (1) and (2) the absorption between ν and $\nu + d\nu$ can be set equal to

$$\frac{C\,d\nu}{\nu^s (e^{h\nu/RT} - 1)} \tag{3}$$

and the number of quanta absorbed is then

$$\frac{C\,d\nu}{h\nu^{s+1}(e^{h\nu/RT} - 1)} \tag{4}$$

Hence the average value of $h\nu/RT$ of an absorbed quantum is

$$\frac{h\nu}{RT} = \int_{x_0}^{\infty} \frac{dx}{x^s (e^x - 1)} \bigg/ \int_{x_0}^{\infty} \frac{dx}{x^{s+1}(e^x - 1)} \tag{5}$$

where $x_0 = h\nu_0/RT$. We shall be concerned only with values of x_0 so large that $(e^x - 1)$ can be replaced by e^x. Hence

$$\frac{h\nu}{RT} = \int_{x}^{\infty} x^{-s} e^{-x} dx \bigg/ \int_{x_0}^{\infty} x^{-s-1} e^{-x} dx$$

$$= \frac{1 - s/x_0 + s(s+1)/x_0^2 - \ldots}{1/x_0 - (s+1)/x_0^2 + (s+1)(s+2)/x_0^3 \ldots} \tag{6}$$

If $\overline{E}$ is the average energy of expulsion and T_0 the initial temperature of the electrons, we have

$$\tfrac{3}{2}RT_0 = \overline{E} = h\nu - h\nu_0$$

so that by (6)

$$\frac{3}{2}\frac{T_0}{T} = \frac{1 - 2(s+1)/x_0 + 3(s+1)(s+2)/x_0^2 - \ldots}{1 - (s+1)/x_0 + (s+1)(s+2)/x_0^2 - \ldots} \tag{7}$$

Hence for large values of x_0, T_0 is approximately $\frac{2}{3}$ T, the next approximation being

$$T_0 = \tfrac{2}{3}T\left((1 - \frac{s+1}{x_0}\right) \tag{8}$$

We notice that this result is quite independent of the degree of dilution of the radiation When there is no dilution there is thermodynamic equilibrium and the electrons must have the equilibrium temperature T, hence they must after expulsion increase in temperature from T_0 to T The secret is that the slowest electrons are quickly weeded out by capture, so that the average energy rises So long as we consider the process (1) to be acting alone there will be the same proportionate weeding out, and the temperature T will be attained irrespective of the dilution of the radiation But when there is dilution the process (2) must be reckoned with,* so that we cannot at present say more than that the process (1) gives a continually renewed supply of electrons with temperature near $\frac{2}{3}$ T, with a tendency to rise automatically to T

For T = 15,000°, RT = 0 86 volts There are no ionisation potentials of importance below 5 volts, so that x_0 is at least 6 and the approximation of setting $(e^x - 1)$ equal to e^x is amply justified We shall show later that interstellar material is likely to be ionised down to 15 volts, giving $x_0 = 18$ Hence by (8) we may well be content with the approximation $T_0 = \frac{2}{3}$ T

9 By the process (2), or rather by its converse, the electrons lose energy during their period of freedom If this loss were rapid the average temperature of the free electrons might well be much below the initial temperature of $\frac{2}{3}$ T No appreciable part of this loss can be recovered by a corresponding absorption because the density of the radiation is far below that required for equilibrium at the temperature π_0 or T The amount of the loss may be estimated by Kramer's theory, this, although explicitly concerned with X-ray frequencies, appears to apply in principle to the analogous phenomena at lower frequencies

If electrons, all of kinetic energy $h\nu_1$, encounter ions the calculated classical spectrum arranged according to ν is of uniform intensity, as shown by the line AB in the diagram The ordinate PM at frequency ν_1 divides the spectrum into two parts, which we shall call α and β Spectrum α is emitted by the converse of process (2), spectrum β by the converse of (1), *i.e.*, by capture of electrons Actually for electrons of uniform initial energy spectrum β breaks up into a line spectrum, but that scarcely concerns us here, in any case the lines will be spread out again by the diverse initial energies Let QPQ′ be a rectangular hyperbola drawn through P with the co-ordinate axes as asymptotes

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* Process (2) acts also when there is no dilution but in that case the principle of separate balancing permits us to derive the temperature from any one process (with its converse) singly

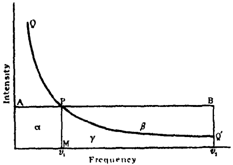

FIG 1

We call the portion of the spectrum Q′PMX spectrum γ The intensity at any point of spectrum γ is to that of spectrum β in the ratio ν_1/ν Now if any electron radiates a quantum $h\nu$ ($\nu > \nu_1$) only the part $h\nu_1$ comes from its energy of motion (The rest is due to its fall to a low potential in the capturing atom) Hence if $h\nu_1$ is the average energy of the electrons in the diffuse matter—

Spectrum β represents radiation emitted by electrons at capture

Spectrum γ represents kinetic energy of electrons preserved until capture and then radiated (along with the remainder of spectrum β)

Spectrum α represents energy radiated by electrons during their free life

The ratio of the energy γ to the energy α is

$$\int_{\nu_1}^{\nu_2} \frac{\nu_1}{\nu}\, d\nu \quad \int_0^{\nu_1} d\nu = \log \nu_2/\nu_1,$$

where ν_2 is the limit at which spectrum β is finally cut off As the logarithm is involved it is unnecessary to fix ν_2 accurately, but it corresponds roughly to the deepest level of capture, say, 10–20 volts Since ν_1 is about 1 volt,* $\log \nu_2/\nu_1$ is about 3 It follows that on the average an electron preserves three-quarters of its original energy until capture, and the average energy during its lifetime is only about 12 per cent below its initial energy

We cannot lay stress on precise figures Our main conclusion is that the electrons tend by process (1) to take up a temperature comparable with the effective temperature of the stars, and although there is sensible cooling by process (2) this does not affect the order of magnitude of the temperature

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* The frequency ν_1 corresponds to the average temperature of the electron gas which we are trying to determine But if, as a first guess, we take ν very low we find the loss of initial temperature very small, so that for the next approximation ν_1 is to be taken as nearly corresponding to the initial temperature. The subsequent approximations then rapidly converge

One rather abstract point may be of interest I think there is nothing in the laws of thermodynamics to prevent the stars from warming up the interstellar medium far beyond their own effective temperatures For simplicity let the material be hydrogen, for which $h\nu_0 = 13\ 5$ volts, and suppose that the spectral lines in the stellar reversing layer absorb all frequencies between 13 5 and 18 5 volts, the star having some clear stretches of continuous spectrum beyond Such a condition is improbable, but is not forbidden by any physical laws Then the electrons expelled by ionisation will all have energy greater than 5 volts and the corresponding initial temperature is above 38,000° It might be urged that this is because the "effective temperature" of the stars becomes misleading when there is so large a deviation from black-body radiation, but it must be noted that the postulated deviation is a deficit not an excess of ultra-violet light

10 An explanation must be added as to the temperature of the atoms At present the position is that if *cool* material were placed in interstellar regions the electrons would take up a temperature of 10,000°, but the atoms would be practically undisturbed by the radiation The temperature of the electrons and atoms must, however, be equalised by the usual process of collisions The important point to notice is that the atoms follow the lead of the electrons and not *vice versa* This is because the supply of hot electrons is continually renewed, whilst the low temperature of the atoms is merely an initial condition which gradually disappears The electron after handing over some of its energy to the cooler atoms goes back for more, the atoms receive the energy and have nowhere to dump it Thus the atoms increase in energy until on balance they receive no more from the electrons

11 The effective temperatures of the stars range ordinarily from 3,000°, to at least 15,000°, and a few stars (of O type) may extend to 25,000° or 30,000° In determining the initial temperature of the electrons very much greater weight must be given to radiation from the hottest sources, since this liberates more electrons in proportion to its intensity The theoretical weights are easily calculated from the theory of § 8, they are proportional to $x_0^2 e^{-x_0}(1 - x_0^{-1} + 2x_0^{-2} + \quad)$ The table shows the weight to be attributed to equal quantities of radiation from sources at temperatures given in the first column, according as the active ionisation potential is at 5, 10 or 15 volts Probably the last column is nearest to the actual conditions

Table III —Weighting of Effective Temperature

Temp	5 2 volts	10 3 volts	15 5 volts
3,000°	10^{-5}	10^{-11}	10^{-18}
6,000	0 05	0 003	10^{-4}
9,000	0 4	0 08	0 016
12,000	1	1	1
18,000	1 5	8	45
24,000	1 3	20	190

Strictly speaking, the hotter sources should be weighted even more highly because the fastest electrons have the longest free life

Giving, then, due weight to the hottest stars, we should find a temperature of the interstellar medium in the neighbourhood of 15,000 to 20,000°

The radiation concerned in establishing this temperature is exclusively of frequency greater than ν_0 If, as we believe, ν_0 is 15 volts, this means wave-length less than 820 Angstroms The question arises whether it is reasonable to assume a black-body law of stellar radiation for a region of the spectrum so far beyond observable limits The latest observations seem to show that the sun obeys the black-body law fairly satisfactorily down to the observable limit at 3,000 A, but the observational verdict is not unanimous, and in any case it leaves a big gap to extrapolate E A Milne showed theoretically that the black-body law will be followed very closely by stars if the absorption coefficient is independent of wave-length, but this result is discouraging rather than otherwise, because we should expect large increase of the absorption coefficient for short wave-lengths But the uncertainty from this cause is not so serious as we might at first suppose Increased absorption in the ultra-violet means that we see less deeply into the star in short wave-lengths, but at the very worst—if there is complete opacity in a thin layer at the surface—we shall receive radiation corresponding to the surface temperature * The surface temperature is only 19 per cent less than the effective temperature

I adopt generally 10,000°, which is probably rather too low even after full allowance is made for the above reduction of 19 per cent and for the reduction of 12 per cent due to process (2)

It is curious to note that the sun's radiation will cool the interstellar gas in its neighbourhood It does this by flooding the gas with comparatively slow-moving electrons

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* This may, however, be modified by absorption lines.

Ionisation in Interstellar Space

12 The usual equations giving the amount of ionisation in terms of temperature and density are clearly inapplicable to the interstellar medium since the equilibrium radiation corresponding to the temperature is not present The radiation differs from equilibrium radiation in two ways (1) It is enormously diluted, (2) it comes from a number of sources at different temperatures We shall for the present ignore the second point and show how to deal with the dilution

Assume then that the stars are all of effective temperature T and that the density of radiation between ν and $\nu + d\nu$ is

$$I(\nu, T)\, d\nu/\delta$$

where $I(\nu, T)$ is Planck's distribution function and δ is the constant "factor of dilution" As shown in the previous section the temperature of the diffuse material will be roughly the same as T

The degree of ionisation is determined by equating the number of captures of electrons to the number of expulsions The former is proportional to the distribution density of the electrons and the latter to the density of the radiation concerned Hence if we multiply electron density and radiation density by the same factor the condition determining the ionisation is unaltered Multiply by δ so as to bring the radiation up to its equilibrium density, the usual equilibrium formula will then apply Hence we have the rule—

The degree of ionisation of the interstellar gas with density ρ is the same as that of a gas with density $\rho\delta$ in thermodynamical equilibrium

This ignores "stimulated captures" proportional to the electron density and radiation density jointly, but these are negligible in the conditions prevailing It also ignores ionisation of excited atoms—which may occur in the comparison gas but not to any extent in the interstellar gas But this only means that the simplest form of the ionisation formula (which neglects excitation) is more accurate for the interstellar gas than for its usual applications

Equilibrium radiation at 10,000° has a density 76 ergs/cm^3 as compared with the density of interstellar radiation $7 \cdot 7 . 10^{-13}$ found in §6 Hence $\delta = 10^{14}$. We should, however, allow for the fact that a large part of the interstellar radiation comes from G and K stars of low weight in regard to ionisation, so that to conform to the assumed average temperature of 10,000° I have adopted

$$\delta = 10^{15}$$

Hence adopting $\rho = 10^{-24}$ (§ 5) we have

$$\rho\delta = 10^{-9}.$$

13. The ionisation-level ψ_0 is calculated from the equation

$$\frac{\psi_0}{\mathrm{RT}} = \log \left\{ \frac{(2\pi m)^{3/2}\, \mathrm{R}^{5/2}\, \mathrm{T}^{5/2}}{h^3 \mathrm{P}_e \delta} \right\} \tag{1}$$

where m is the mass of an electron, h Planck's constant, R Boltzmann's constant, and P_e the pressure of the electron gas. Weight-factors, symmetry numbers, and minor complications depending on the particular type of atom are neglected; excitation is also neglected, but this is justifiable since ψ_0/RT turns out to be large. The factor δ is introduced as explained in § 12, the density of the material being involved in P_e.

Electrons at an energy level ψ_0 are half ionised and half not. For electrons of ionisation potential ψ, the fraction ionised (x) is given by

$$x/(1 - x) = e^{(\psi - \psi_0)/\mathrm{RT}} \tag{2}$$

Allowing one free electron to every 20 units of atomic weight (*e.g.*, Na_+, Ca_{++}, or Fe_{+++}) we find—

$$\psi_0/\mathrm{RT} = 18{\cdot}2 \qquad \psi = 15{\cdot}7 \text{ volts}$$

There is an increase of 1·98 volts for each factor of 10 by which $\rho\delta$ is decreased. Uncertainties as to density and dilution factor are therefore of minor importance. Changes in T make a considerable difference; between 5,000° and 20,000° ψ_0 changes nearly proportionately to T. Hence ψ_0 may well be in error by ± 5 volts.

14. In the foregoing discussions we have implicitly assumed that the interstellar medium is sufficiently transparent to the short wave length radiation effective in ionisation. This radiation is, however, absorbed in the process of expelling electrons, and our assumption implies that the rate of recapture of electrons is so slow that the ionising radiation can do what is necessary without itself being appreciably weakened. This requires justification because most discussions of the transparency of space refer to visual light which is not subject to this form of absorption.

If the absorption coefficient were very high so that all ionising radiation were removed from starlight in the first few parsecs of its track, we should have to reconsider the dilution factor δ. Our value 10^{15} was based on the observed visual intensity of starlight (1,000 first magnitude stars), but if the light has been robbed of its high frequency constituents δ may be almost infinite. This, however, greatly exaggerates the possible modification because there is a compensation; the ionising radiation removed from the direct stellar beam will be restored as diffuse radiation of the sky. Its energy is passed on to a free electron which must ultimately be captured, and the capture will release a quantum of ionising radiation It is true that such absorption and re-emission, if it occurs in the *immediate neighbourhood* of a star, checks the outward flow by turning back some of the radiation on to the star itself, but when it occurs in regions where the star no longer subtends a considerable solid angle, the double process makes no difference to the density of radiation in space

Owing to this compensation the absorption would scarcely concern us were it not for process (2) This makes the average speed of electrons lower at capture than at expulsion, so that the emitted quanta are of lower frequency than those absorbed, and they will tend to expel electrons with less energy The first electron may thus have a succession of lineal descendants starting off with smaller and smaller energy In fact the loss by process (2) is not limited to the life of one electron, though it is not passed on from one free life to the next, it is transmitted from parent to offspring We have hitherto recognised only the one primary source of interstellar radiation—the direct radiation of the stars, radiation which has been once absorbed and remitted will form a secondary source, radiation twice absorbed and re-emitted a tertiary source, and so on Presumably each successive source has a lower equivalent temperature We have assumed that these subsidiary sources are comparatively weak

According to Kramer's theory the emission per cubic centimetre per second between frequencies ν and $\nu + d\nu$ is*

$$ns\,d\nu\,\frac{32\pi^2}{3\sqrt{3}}\,\frac{z^2e^6}{c^3m^2\nu}$$

where n and s are the numbers of electrons and ions per cubic centimetre, e, m, ν the charge mass and mean speed of an electron, c the velocity of light, and ze the effective charge of the ion The formula should be valid up to frequencies of 15 volts if the atoms are mostly ionised to that level

For density 10^{-24} we have roughly $ns = 0\ 002$ Taking $z = 3$, $\mathrm{T} = 10{,}000°$, the emission is

$$10^{-41}\,d\nu\ \text{ergs/cm}^3\,\text{sec} \tag{1}$$

As already explained, the absorption is not exactly equal to the emission, but it will be of the same order of magnitude By Planck's law the energy-density due to the stellar sources for $\mathrm{T} = 10{,}000°$, $\delta = 10^{15}$, $h\nu = 10$ volts, is found to be

$$10^{-30}\,d\nu\ \text{ergs/cm}^3, \tag{2}$$

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* See 'Monthly Notices,' vol. 84, pp. 106–7.

so that the average free path of the radiation is 10^{11} seconds or 3 000 light years.

If this result is right the transparency is high enough to justify the treatment adopted in §§ 9–13. But considering the large uncertainties both of theory and data the margin is not very ample. This contingency really requires much fuller investigation than I have been able to carry out but we shall presently see that the conclusion is supported by the transparency of the bright nebulæ.

It should be noticed that for frequencies between 5 and 15 volts the medium has no regular absorption coefficient in the ordinary sense of the term. The absorption in each cubic centimetre is limited to about $10^{-41} d\nu$ ergs per second irrespective of the quantity of radiation flowing through it. Accordingly in the neighbourhood of a star the absorption will be very small in comparison with the large amount of radiation transmitted that is to say the absorption coefficient will be decreased.

The absorption is proportional to *ns* and therefore to the square of the density. Hence in a nebula it would be 10^8 times larger than in interstellar space. In a bright nebula this will not lead to an unduly high absorption coefficient because the hot stars in the nebula provide extra intensity of radiation that is to say the quantity (2) is considerably increased as well as the quantity (1). In fact we can see immediately that a bright nebula must be fairly transparent to radiation of energy 12 volts this is required to excite the Balmer series. Conversely we can argue from the actual transparency of the nebulæ that our result for interstellar space is not too high.

Applying the same calculation to a dark nebula the absorption would be the same as in a bright nebula but the absorption coefficient much higher (10^8 times greater than in interstellar space). It is possible therefore that most of the radiation within the dark nebulæ has been many times absorbed and re-emitted. The extended operation of process (2) then comes into play and the temperature both of the radiation and of the material may be comparatively low. The high absorption coefficient has no reference to visual light so that it does not afford an immediate explanation of the well known obscuring power of dark nebulæ, but the consequential low temperature may play a part in the visual opacity (see § 19).

PART II.—ASTRONOMICAL CONSEQUENCES

Absorption Spectrum of Interstellar Matter

15 Since excited atoms will be exceedingly rare the only absorption lines of considerable strength will be *principal lines*, *i e*, lines absorbed by the unexcited atom or ion

We consider first the abundant elements sodium and calcium Na, Ca and Ca_+ all have principal lines in the observed part of the spectrum, but the more highly ionised atoms of these elements have none, and will be undetectable

We shall adopt $\psi_0 = 20$ volts, since this gives a rather more favourable comparison with observation than the value 15 7 reached in § 13 This corresponds to a temperature of the interstellar medium about 12,000°, which is perhaps the most likely

The first two ionisation potentials of sodium are 5 1 volts, 30–35 volts With $T = 12{,}000°$, $RT = 1$ 03 volts Hence by § 13 (2)

$$\begin{aligned} x/(1-x) &= 2 \quad 10^6 \text{ for the first ionisation} \\ &= 10^{-6} \text{ for the second ionisation} \end{aligned}$$

Thus the sodium is nearly all Na_+ (which is undetectable), but there is one part in 2,000,000 of Na

The first two ionisation potentials of calcium are 6 1 volts, 11 8 volts. Hence

$$\begin{aligned} x/(1-x) &= 7 \quad 10^5 \text{ for the first ionisation} \\ &= 3 \quad 10^3 \text{ for the second ionisation} \end{aligned}$$

The calcium is nearly all Ca_{++}, but there is one part in 3,000 of Ca_+, and one part in 2,000,000,000 of Ca

We notice that there is much less un-ionised calcium than sodium Ordinarily in thermodynamic equilibrium we expect less sodium because it has the lower ionisation potential The reversal here found is not due to the departure from thermodynamical equilibrium, but *to* the *extreme conditions of* temperature and density which make the second ionisation potentials take a hand in the results *

The terrestrial abundance of calcium is a little more than 1 per cent Assuming that this applies also to interstellar material, we shall have 10^{-26} gm of Ca_{++}

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* This explanation of the occurrence of neutral sodium without neutral calcium is essentially the same as has been advanced by R H Fowler and others, the detailed figures will perhaps help to make it convincing

and $3\ 10^{-30}$ gm of Ca_+ per cubic centimetre A column of 1 square centimetre section and length 100 parsecs ($3\ 10^{20}$ centimetres) will contain 10^{-9} gm of Ca_+

The monochromatic absorption coefficient of Ca_+ is found from E A Milne's investigation of the equilibrium of the calcium chromosphere The result is $k = 9\ 10^8$ The chief uncertainty arises from the assumed width of the lines, Milne adopts one Angstrom for the combined width of the H and K lines which is perhaps rather excessive for the rarefied atmosphere As the method determines the total absorption in the lines, k may be rather larger if they are concentrated into small width However, with $k = 10^9$ and 10^{-9} gm of Ca_+ per 100 parsecs, the H and K light will be reduced $1/e$ or about one magnitude per 100 parsecs These lines should therefore appear in the spectrum of light which has traversed more than 100 parsecs

The proportion of neutral sodium is 1/2,000,000 against 1/3,000 for Ca_+, so that it is relatively 700 times less abundant Sodium atoms are about three times as numerous terrestrially as calcium atoms, so that the figure may be reduced to 200 I understand from R H Fowler that the monochromatic absorption coefficient for the D lines is not likely to be greater than for the H and K lines Our calculation therefore suggests that the sodium spectrum will be very much weaker than the ionised calcium spectrum, on the other hand we shall find that the observations indicate no great difference in the intensity

The gap is not closed up by any likely modification of T or ψ_0, but it may be somewhat diminished if we take account of the diverse temperatures of the stars In substituting an average temperature we diminish the quantity of high frequency radiation and increase the low frequency radiation Table III shows that radiation at 12,000° and 24,000° produces nearly the same ionisation at 5 2 volts (Na), but ionisation in the ratio of 1 to 20 at 10 3 volts (roughly Ca_+). Our ionisation formula, § 13 (1), assumes evenly diluted black-body radiation, and if allowance were made for the greater abundance of high frequencies we should obtain more double ionisation of calcium and less single ionisation of sodium. This correction will make the H and K absorption somewhat less than stated above

Evidently the intensity of neutral Ca is very much weaker and the spectrum will be undetectable within the limits of the stellar system

I am not qualified to discuss other elements in detail, but I think that physicists have satisfied themselves that none will rival calcium and sodium Either the elements are less abundant terrestrially or those ions which have principal lines in the observable spectrum are absent for the same reason as neutral calcium *

Fixed Calcium and Sodium Lines

16 In some spectroscopic binaries the H and K absorption lines do not partake of the orbital motion shown by the other lines Clearly these "fixed lines" are not formed in the reversing layers of either component The D line also is sometimes stationary, but no other stationary lines have been found

This fixed absorption might be produced either in a special cloud surrounding the binary system not connected with either component in particular, or in the general interstellar medium If the cloud is a special one permanently attached to the star the H and K velocity must be the same as that of the centre of mass of the binary An extensive investigation by J S Plaskett† has shown that in general the velocity differs Plaskett measured the ordinary radial velocity and the calcium velocity of 40 stars of types O to B3, and found often large differences ranging up to 40 km per second or more The sodium velocity agreed fairly closely with the calcium velocity Moreover, after correcting for solar motion the calcium velocity was reduced nearly to zero, whilst the stars often had large individual velocities The results were therefore inconsistent with the hypothesis of separate clouds moving with the individual stars, but were consistent with the view that the absorption of the calcium and sodium lines occurs in a continuous cloud pervading the galactic system, nearly at rest relative to the mean of the stars and with little (but not necessarily zero) relative portion of its parts

This would have seemed to settle the whole question but for one grave difficulty The fixed lines have not been found in any stars of type later than B3 If they are formed in interstellar space they should, of course, be present in all stars as distant as those used in Plaskett's investigation

17 Undoubtedly the detection of fixed lines in stars later than B3 would be difficult In B5 and later types Ca_+ occurs in the reversing layer or chromosphere, so that true stellar lines are formed which will mask the fixed lines unless there is a large difference of radial velocity From types F to M the H and K lines of the star itself are so intense and broad that search for the fixed lines is hopeless It must be remembered also that not many stars attain the high intrinsic luminosity of types O—B3, so that most of them are ruled out

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* In the discussion on the lecture Sr_+ was mentioned as a possibility According to C H. Payne the terrestrial abundance of strontium is 0 0065 per cent, against 1 5 per cent. for calcium, so that it is heavily handicapped.

† 'Monthly Notices,' vol. 84, p 80; 'Pub Dom Obs Victoria,' vol 1, pp. 163 and 287

by insufficient distance The average radial velocity of types B5—B9 is exceptionally low, and it would be difficult to find stars with sufficient speed to separate the stellar and fixed lines The blending of the two sources of absorption has been observed in some spectroscopic binaries, that is to say, the blended H and K lines oscillate with the same period and phase as the pure stellar lines but with reduced amplitude *

The failure to detect the lines in types later than B3 is therefore to be explained in one of the three ways (1) masking by broad stellar lines, (2) insufficient radial velocity, (3) insufficient distance. The most difficult case is one given by Frost and Struve † The star 66 Eridani, type B9, mag 5 2, is a spectroscopic binary with a maximum relative velocity of the components amounting to 220 km per second There is therefore plenty of room for the fixed K line to appear *between* the stellar lines, but none are detectable The distance is probably about 100 parsecs (an estimate based on the probable absolute magnitude of a star of type B9) We must presume then that this distance is insufficient to give detectable absorption

Mention must be made of an alternative attempt to account for the association of fixed calcium with the hottest stars only It is suggested that the absorption although occurring in the interstellar cloud is controlled by the hot star, the stellar radiation being required to ionise the calcium This is, of course, directly contrary to our conclusion in § 15 as to the state of ionisation of the medium, proximity to a very hot star would decrease the amount of Ca_+ by causing more double ionisation But a more direct objection is that the explanation clearly does not apply to the fixed sodium lines which are absorbed by neutral excited sodium

It might also be suggested that the general cloud consists mainly of elements more primitive than sodium and calcium, and that these elements only occur in proximity to hot stars from which they are expelled by radiation pressure I do not see how a star moving through the cloud at, say, 30 km per second, can prepare a stationary smoke-screen ahead of it The "smoke" cannot be so dense as the cloud (otherwise the motion would be that of the star not the cloud), and it therefore seems impossible that there should be enough stationary sodium near the star to produce the required absorption In any case the absorption should be much more intense for receding stars than for approaching stars, I do not think that any such correlation is shown in the observations.

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* It has sometimes been supposed that this indicates a cloud surrounding the system which sways with the motion of the heavier component in the same phase but with enfeebled amplitude, but I do not know of any suggestion as to how such a motion could be produced Pressure effects of the motion of the star would be transmitted with a phase-lag of weeks or months

† 'Ap. J.,' vol 60, p 313

The simple theory that the lines are produced by regular absorption in the interstellar cloud is supported by the investigation of § 15, which shows that it is fairly satisfactory quantitatively We there found an H and K absorption of about 1^m per 100 parsecs, but later decided that the estimate ought probably to be reduced (In any case the uncertainties of the calculation allow some elasticity) If we make it 1^m per 500 parsecs we escape the difficulty of 66 Eridani Many of Plaskett's stars are distant 500-1,000 parsecs Some of the Orion stars which show the fixed lines are much nearer, but these are in the Orion nebula and their light passes through denser material There is no need for so great a distance when the star is in or behind a diffuse nebula

It is also in accordance with our theory that fixed sodium is not so often observed as fixed calcium, though the observed difference is scarcely so great as we should expect

Scattering of Light in Space

18. The *line absorption* already investigated has insignificant effect on the observed brightness of the stars *Continuous absorption* is caused by—

(1) *Ionisation* —This only concerns the invisible ultra-violet region far beyond the observable limit

(2) *Switches of Electrons at encounter with Atoms* —Since an atom only meets an electron about once in five days its absorbing power by this method is exceedingly small

There is more hope of effects being produced by scattering—especially electron scattering But with density 10^{-24} and one electron for every 20 units of atomic weight, we have one free electron in 30 cubic centimetres, or 10^{-19} electrons per square centimetre per 100 parsecs, these altogether obstruct 6 7 10^{-6} square centimetres, that is to say, the scattering coefficient is—

$$0\ 0000067 \text{ per 100 parsecs}$$

Thus the dimming of even the most distant stars is negligible

The Rayleigh scattering by atoms and ions is much smaller We can see this by the following comparison The scattering coefficient of electrons in *fully ionised* matter is $\frac{1}{5}$, that is to say, 5 gm per square centimetre will reduce the radiation in the ratio $1/e$ or 1 magnitude We have above us 1,000 gm per square centimetre of atmosphere, so that if the atmosphere were fully ionised the light of a star overhead would be reduced 200 magnitudes, if singly ionised the reduction would be 14 magnitudes The Rayleigh scattering for ions is practically the same as for neutral atoms, *i e*, the actual atmospheric scattering, this is much less than 1 magnitude We see therefore that in ionised material (even if singly ionised) the electron scattering is much greater than the ion scattering

Accordingly it appears that ordinary regions of space will have nearly perfect transparency, and the usual assumption made in deducing the distance of remote objects is justified So far as we can see the only possible pitfall is the possible existence of quantities of meteoric matter

The assumption that interstellar space is nearly transparent has usually been based on Shapley's observation that the light of the stars from the most distant globular clusters is not appreciably reddened It is held that dimming without reddening is impossible (unless the obstruction is by solid meteoric particles of considerable size) In our opinion this argument is fallacious,* since it applies only to un-ionised gas, whereas interstellar gas must necessarily be ionised Electron scattering affects all optical wave-lengths equally and does not redden the light, and we have seen that in ionised material it far outweighs the Rayleigh scattering †

19 One grave difficulty remains how are we to account for the obscuring power of the dark nebulæ? We have seen that the density at the centre of these nebulæ is about 10^{-20}, and indeed, apart from the theory of isothermal equilibrium, we are unable to attribute much higher density without arriving at so high a mass as to disturb stellar velocities in the neighbourhood For density 10^{-20} the scattering coefficient is 0 067 per 100 parsecs, so that a nebula of diameter 10 parsecs cannot appreciably obscure the stars The observed dimming in a typical case amounts to 2 magnitudes‡, it seems impossible to strain the theoretical calculation so as to give anything like so large an amount The only way of obtaining the obscuration with the mass at our disposal is by taking it to be in the form of fine solid particles I have great reluctance (which is perhaps a prejudice) to admit meteoric matters of this kind in interstellar regions, but I cannot suggest an alternative

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* It was perhaps justified at one time when interstellar matter was pictured as a dust cloud, but seeing that the forms of matter in space actually known to us are nebulous gases and meteoric masses, it is difficult to understand why the intermediate form of dust should be specially selected for consideration

† This was pointed out to me in 1923 by S Rosseland.

‡ A Pannekoek, 'Proc Akad Amsterdam,' vol 23, p 720 Pannekoek points out the difficulty as to the mass, but he assumes only Rayleigh scattering The difficulty is reduced but not eliminated by introducing electron scattering

It should be noticed that if we admit meteoric matter in order to explain the dark nebulæ there is no safeguard that other regions of the sky will be as transparent as is generally assumed

[I was rather glad to find that my prejudice against meteoric matter was shared by others in the discussion on the lecture One suggestion offered was molecular absorption It is difficult to admit the existence of molecules in interstellar space because when once a molecule becomes dissociated there seems no chance of the atoms joining up again The atoms will by ionisation lose their valency electrons and consequently lose their power of chemical combination, in fact the resulting positive charges will tend to hold them apart

If this seemingly fatal objection is overruled the calculations are not unfavourable to molecular absorption as the cause of the opacity of dark nebulæ The energy density of radiation in space (§ 6) corresponds to about one visual quantum in 3 cubic centimetres At the centre of a nebula the density 10^{-20} would provide about 50 molecules in 3 cubic centimetres, so that by a concerted effort the molecules could absorb fifty times over all the starlight lying about It is sufficient that each molecule should function once in 500 years, this will give complete extinction of all light in transit across the nebula once in 10 years, that is to say light traverses an average thickness of ten light years (3 parsecs) before absorption—roughly the required opacity The molecular absorption, if any, corresponds to dissociation and not to band spectrum, since band absorption in the visual region would presumably have been detected spectroscopically Consequently it is necessary that the molecule should be disrupted and reformed once in 500 years—not an extravagant demand, since atomic collisions in the nebula are much more frequent than in interstellar space (§ 4) We can, in fact, safely allow a large proportion of the molecules to be idle

On this hypothesis the absorption per unit volume is proportional to ρ^2, since it depends on the number of recombinations of pairs of constituents, the nebula is thus 10^8 times more opaque than an ordinary region of space Further, the bright nebulæ will be more transparent than dark nebulæ, because the bright stars in the former dissociate the molecules by their radiation

Possibly the way out of the difficulty lies in the suggestion at the end of § 14 that the temperature may be comparatively low in dark nebulæ. According to that discussion the temperature may well be so low that ψ_0 falls below 5 volts In that case the atoms are mostly un-ionised, and there is no obstacle to the formation of molecules and consequent molecular absorption But ought we not in that case to find some traces of band spectr in stars which are partially dimmed by the nebula ?]

Accretion of Stellar Mass

20 A star moving through the interstellar medium will sweep up the matter near its track It is important to estimate the amount of this accretion

It seems necessary to distinguish the cases in which the velocity of the star is greater than or less than the velocity of sound in the medium which is about 4 km per second Taking the ordinary case in which the velocity V of the star relative to the medium is greater than the velocity of sound there can be no compressional wave travelling in front of the star and the only force affecting the gas as it flows to meet the star is the gravitational attraction of the star The mutual collisions of the particles have then no important effect and we neglect them in the following analysis *

Consider a particle which would if undisturbed have passed the star at distance σ so that its angular momentum is σV Let it be deflected so as to pass actually at distance *d* its velocity at nearest approach being V′ Then conservation of energy and angular momentum gives

$$\tfrac{1}{2}V'^2 - \tfrac{1}{2}V^2 = GM/d$$

$$V'd = V\sigma$$

Hence

$$\frac{\sigma^2}{d^2} = 1 + \frac{2GM}{V^2 d} \tag{1}$$

If we take *d* equal to the radius of the star σ will give the radius of the circular cylinder swept by the star Note that *d* may not be the ordinary radius of the star it must include coronal appendages sufficiently dense to entangle passing atoms

In practical cases $2GM/V^2d$ is large hence with sufficient accuracy—

$$\sigma^2 = 2GMd/V^2 \tag{2}$$

and the rate of accretion of mass is

$$\frac{dM}{dt} = \pi\sigma^2 V\rho = 2\pi GM\rho d/V \tag{3}$$

ρ being the density of the cloud (10^{-24})

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* The collisions are between particles having the same general velocity apart from the small individual velocities averaging about 3 km per second. If there were a compressional wave travelling in front of the star there would be collisions of particles of widely different motion many of the oncoming particles would be arrested in their motion and drop towards the star

For the sun $M = 2\ 10^{33}$, $V = 2\ 10^{6}$, $d = 7\ 10^{10}$ Hence

$$\frac{dM}{dt} = 3\ 10^{7} \text{ gm per second.}$$

Here only the ordinary solar radius is allowed for, and we may perhaps multiply by a factor 5 to allow for the catching power of the corona, or even a factor 50 on account of the zodiacal light But in any case the accretion is very much smaller than the sun's loss of mass by radiation which amounts to 4 2 10^{12} gm per second

It is clear also that the resistance offered by the medium is small The momentum of 30 tons per second at a relative velocity of 20 km per second cannot cause much stoppage, and at the present rate the sun's mass will have disappeared by radiation before there is a retardation of anything like a kilometre per second

I have examined other stars but in no case does the accretion approach the loss of mass by radiation

The complete cleaning up of space can never be accomplished in this way The mass to be swept is about the same as the mass of the stars, and since these lose mass faster than they sweep it they cannot live long enough to complete their task This disposes of a possible argument that a diffuse cloud in space is inconsistent with the cleaning activities of the stars

21 In the thickest part of a diffuse nebula the density is 10,000 times greater than in ordinary regions, and it is possible that accretion may counterbalance radiation of mass This balance is of no serious interest if it is merely a temporary arrest of evolution of a star whilst passing through the nebula, but it may be of great importance for stars which are permanently in the nebula The latter must necessarily be moving slowly relative to the nebulous material (the only motion being orbital motion under the attraction of the mass of the nebula) The slow velocity helps the accretion of mass in accordance with § 20 (3) I suppose that when the velocity is less than the velocity of sound the accretion changes (perhaps discontinuously) to a much greater rate, but I have not been able to tackle this problem analytically

It seems likely therefore that for slow moving stars in nebulæ evolution by change of mass is arrested or even reversed A star so situated would perhaps grow in mass until it reached a determinate size for which the rate of radiation of mass overtook the rate of accretion. I suggest that the association of the massive B stars with nebulæ and with low individual velocity is due to this cause * It will be seen that this inverts the usual idea that the high mass is somehow responsible for the low velocity, it is the low velocity (coupled with other conditions) which is responsible for the high mass

The orbital velocity within a nebula is easily calculated from the theory of the isothermal gas-sphere (§ 5) If V is the velocity in a *circular* orbit at distance r from the centre,

$$V^2 = -r\frac{d\phi}{dr} = \kappa\left(-z\frac{du}{dz}\right)$$

where $\kappa = P/\rho$, P being the pressure † If V is the velocity of sound, we have

$$U^2 - \tfrac{5}{3}\frac{P}{\rho} = \tfrac{5}{3}\kappa,$$

so that

$$V^2/U^2 = \tfrac{3}{5}\left(-z\frac{du}{dz}\right)$$

The following values of $-z\,du/dz$ are found from Emden's Table —

$z =$	1	2	3	4	5
$-z\,du/dz =$	0 304	0 946	1 55	1 98	2 24
$V/U =$	0 33	0 75	0 99	1 08	1 16

Referring to the corresponding table of densities in § 5 we see that the circular velocity of a star is less than the velocity of sound in any part of the nebula where the density has not fallen below one-third of the central density The velocities of stars in the conspicuous part of the nebula should, therefore, not exceed 4 km per second

It may be objected that the velocities of B-type stars, although small, average considerably more than 4 km per second But the average includes some accidental B stars which have no relation to nebulæ Moreover, the 4 km per second refers to motion relative to the nebula, and the nebula is not necessarily devoid of individual velocity

Evolution of Nebulous Condensations

The isothermal equilibrium of nebulous condensations has been considered in § 5 for the purpose of estimating the density of interstellar matter The mathematical results are so curious that I can scarcely refrain from following them a little further—if only as an abstract problem It is obvious that an actual irregular nebula, evidently distorted by conflicting currents, is very crudely represented by a static spherical distribution, and the representation was only intended to furnish a rough estimate of the scale of the condensations—it being presumed that the pressures and gravitation potentials must be of the same order of magnitude in irregular as in symmetrical distribution. But it happens that the problem of spherical condensations admits of unexpectedly definite development. I could scarcely justify an expectation that the more remote conclusions will be applicable to the actual universe; however, they will be given here as they follow from the idealised premises.

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* This is not intended to over rule another cause of association, viz., that the hot B-type stars cause the nebula to shine and so become recognisable

† Acquaintance with Emden's discussion (*loc cit.*) is here presumed

In § 5 we assumed an average separation of the nebulæ such that a random point might be expected to be 150 parsecs from the nearest nebula, and then deduced a density 10^{-24} at such a point. A theory of evolution of the condensations should proceed in the reverse direction. Accordingly we first *assume* a continuous medium of density $3 \cdot 10^{-24}$ and examine how it will begin to condense. (This primitive density is chosen higher than 10^{-24} because the normal regions will be drained of matter in order to form the condensations.) We assume as before $T = 10{,}000°$ and $\mu = 1.0$; this means that we do not go quite back to the beginning of things, since some stars must already have been evolved in order to produce the high temperature and ionisation.

No finite isothermal mass can be in equilibrium; it seeks ultimately to diffuse away to infinity. We postulate that our medium as a whole hangs together whilst the condensations are proceeding, either because the transfer of mass over great distances takes time, or because the temperature falls off towards the boundary where no stars exist, or because space is curved, etc. Obviously condensations will occur if they can, because they diminish the potential energy. We suppose a number of condensations to start, and these, being on a comparatively small scale, will strive to settle down to an equilibrium isothermal distribution.

We might suppose that such a condensation, if given the chance, would draw in matter without limit and increase indefinitely; but curiously enough this is not so. No mass is drawn in from outside a sphere of radius R, where R cannot be greater than 158 parsecs or less than 136 parsecs. If during the growth of the condensation matter has flowed in from beyond R, it will be found out again when the equilibrium pressure is finally established. Naturally it will then go to augment other condensations or form the nucleus of a fresh condensation. We can picture a long process of "trial and error" occurring before all the condensations are happily settled with no matter left homeless. We can readily understand how the nebulæ become distorted into irregular forms as the superfluous matter is bandied from one to another condensations will start only to find that other condensations have intersected their sphere and are draining away the matter

The limits 158 and 136 parsecs are found in Table IV

Table IV

ρ		$3\,du/z\,dz$	ρ_0	r	ρ_R	R pc	Ω/M
$8\ 10^{-24}$	3	0 5162	$5\ 8\ 10^{-24}$	0 024	$2\ 00\ 10^{-24}$	127	0 021
	10	0 07736	$4\ 0\ 10^{-23}$	0 0631	0 96	158	0 180
	30	0 00694	$4\ 3\ 10^{-22}$	0 208	0 81	144	0 315
	50	0 00230	$1\ 3\ 10^{-21}$	0 361	0 88	138	0 326
	100	0 000563	$5\ 4\ 10^{-21}$	0 736	0 95	136	0 316
	300	0 0000653	$4\ 6\ 10^{-20}$	2 14	1 08	140	0 252
	1 000	0 00000613	$4\ 9\ 10^{-19}$	7 00	1 00	143	0 257

The table is calculated as follows Since R is the radius of the sphere such that no mass has entered or left the mean density ρ within R is the original density of the uniform medium If z and u correspond to R it is easily shown that $\rho/\rho_0 = 3\,du/z\,dz$ and this quantity is accordingly computed from Emden s table Hence for a series of assumed values of z we obtain the values of ρ_0 tabulated—indicating different degrees of condensation The actual density ρ_R at distance R is given by $\rho_R = \rho_0 e^{u}$ As before $z = (10^{30}\,\rho_0)^{\frac{1}{2}}\,r$ the factor depending only on the temperature and molecular weight r is measured in parsecs Since the tabulated value of z refers to $r = $ R we can determine R The last column will be explained presently

The fluctuations of R down the column are quite real and a more extended table shows that the maxima and minima occur very close to $z = 10$ 100 1 000* thus the limits are 158 and 136 parsecs as stated (The first entry giving R less than 136 can scarcely be called a nebulous condensation since the density at the centre has only been increased twofold) We can thus fix very accurately the average separation of the condensations since matter lying outside the sphere of one must find its way into another condensation in the final equilibrium Of course some compromise must be effected in the packing together of the spheres of condensation

The radius and mean density being given we can calculate the total mass M of the condensation The limits are 470 000 and 730 000 times the sun s mass This sets a limit to the number of stars which can form a star cluster If I am right in believing that the masses of the stars *when first formed* are generally about $3 \times \odot$, the number can scarcely exceed 100,000, for presumably only the denser central part of the nebula will tend to break up into stars *

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* Presumably the series continues with rapidly decreasing amplitude of oscillation.

We ask next whether there is any preference for one degree of concentration rather than another The medium will tend to distribute itself so as to have the lowest possible potential energy Let Ω_1 be the negative potential energy of the mass M of the condensation (considered as isolated), and Ω_2 its original negative potential energy when in the form of a uniform sphere The mutual energy in respect of surrounding material will be the same for both The decrease of energy is then $\Omega = \Omega_1 - \Omega_2$ As the different forms of condensation have different masses we must compare the values of Ω/M I find that—

$$\Omega/M = 3\kappa\left(1 - \frac{z\,dz}{3\,du}e^{u} - \frac{1}{6}\frac{z\,du}{dz}\right)$$

The values (omitting the constant factor 3κ) are tabulated in the last column of Table IV The maximum occurs very near to the value $z = 50$, and we suppose accordingly that this form of condensation will ultimately tend to prevail The unit of z is then 2·75 parsecs, and referring to the law of decrease of density already given in § 5, the density falls to one third of the central value in 8 parsecs and to $\frac{1}{10}$ in 20 parsecs This is more or less the typical extension of diffuse nebulæ, but I should judge that it rather exaggerates their size

In applying these results to the actual universe we must allow for considerable dissimilarity from the idealised conditions and not lay too much stress on small differences of Ω/M The inference which I would draw is that condensations will have a strong tendency to deepen to a form corresponding to about $z = 50$, since this gives large reduction of energy, but they do not tend to deepen indefinitely There is limit—which should be at $z = 50$ according to the idealised calculation but is probably nearer $z = 100$ in actual conditions—beyond which there is no advantage as regards energy

We naturally proceed to discuss sub-condensations formed in the primary condensation The problem is the same except that we have to start with a density, say, 10^4 times greater This makes the linear scale 10^2 times smaller, so that the sub-condensations drain spheres of radius 1·36 parsecs and have a mass $4700 \times \odot$ The distance would do well enough for the average separation of the stars, but the mass is altogether too high

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* If in accordance with later conclusions we take the form for $z = 100$, one-sixth of the whole mass is concentrated within a sphere of 13 parsecs radius.

The failure is not surprising when we remember that the predicted density at the centre of the sub-condensations would be about 10^{-17}, and the conditions have become altogether different from those of diffuse matter at density 10^{-24} In particular the temperature will fall and the matter cease to be ionised as explained in § 14 It would not be extravagant to adopt $T = 500°$, $\mu = 50$ Then κ would be reduced to 1/100th, the linear scale reduced to 1/10th, and the masses of the condensations reduced to 1/1000th We should thus have stars of mass 4 7 × ☉ and average separation 0 14 parsecs, the separation is not too small for stars supposed to be formed in a dense cluster But these figures are of no real importance because the isothermal theory has evidently collapsed for the sub-condensations I remain of the opinion that I have long advocated, namely, that it is radiation pressure which finally settles the masses of the stars

The steps in the formation of a star would seem to be somewhat as follows As the density of the sub condensation increases, its centre becomes opaque to ionising radiation and the temperature falls, probably to a very low value This brings about opacity to visual radiation, even if the theoretical reason is doubtful, we can refer to the observational evidence of the visual opacity of dark nebulæ Consequently, although now of low temperature, the matter has the potentiality of rising to high temperature because it can retain heat generated within it by contraction By the time it has again reached 10,000° a great increase of density will have occurred and there is no danger of losing its opacity An important phase is reached when the density is great enough to intercept and scatter penetrating radiation from sub-atomic processes and so secure an additional supply of heat We have deemed this source unimportant in the nebulæ and in the general interstellar medium, since the sub-atomic energy liberated in them will escape in the unutilisable form of penetrating radiation Without attempting to follow the steps in detail we may note the following points —

(1) The above development refers to a small area in the condensation and proceeds comparatively rapidly or perhaps catastrophically, its evolution breaks away from that of the condensation as a whole (It takes about 200,000 years for a pressure wave to traverse the whole condensation)

(2) As soon as the opacity is sufficient to secure radiative equilibrium radiation pressure becomes important Owing to the high molecular weight this keeps the mass very low at first (well below the sun's mass), but afterwards as the internal temperature rises and intense ionisation occurs more is allowed to accumulate

I can scarcely hope that in this study of diffuse interstellar matter all the essential elements have been recognised and taken into consideration So big a subject can only be attacked piecemeal I hope that the lecture, however incomplete will help to fix ideas as to some of the features of the problem

The Continuous Spectrum of Mercury Vapour in relation to the Resonance Line 2536 52

By Lord Rayleigh, F R S

(Received May 28, 1926)

[Plate 8]

In a former paper* it was shown that the continuous spectrum of mercury vapour started as nearly as could be observed from the resonance line 2536 52 $1S-1p_2$, and stretched without intermission from that point to the green region, where it is most conspicuous This spectrum was obtained by allowing the glowing mercury vapour distilled from the arc to mature by passing it through a long tube, or alternatively by the discharge of an induction coil through mercury vapour which was distilling continuously from the mercury surface, used as cathode of a wide discharge tube The effect is shown in No I, Plate 8, reproduced for convenience of reference from that paper

It can hardly be doubted that the continuous spectrum is intimately associated in some way with the resonance line $1S-1p_2$ For instance, resonant excitation by the light of this line excites the continuous spectrum as well; in the distillation experiment this line and the continuous spectrum *together* become more prominent relative to all other lines as the luminous vapour matures, and the excitation potential appears to be nearly or exactly the same for each †

To help in elucidating the nature and origin of the continuous spectrum, it is evidently important to determine, as exactly as possible, the position of its limit near the line 2536 52 This and other kindred questions are discussed in the present paper

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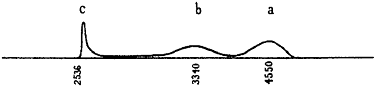
* 'Roy. Soc Proc,' A, vol 108, p 262 (1925).

† Grotrian, 'Zeit. f Phys,' vol 5, p. 148 (1921).

When the continuous spectrum was obtained in either of the ways mentioned, the line 2536 52 was exceedingly strong in comparison with the continuous spectrum and the other series lines. The blur of photographic over-exposure surrounding this line made it impossible to examine the exact position of the limit. A method was therefore sought for getting the continuous spectrum without the line, and it was found in fluorescent excitation of the vapour by the aluminium spark. The spectrum got in this way has already been studied by Wood and others,* but these authors do not seem to have recognised that the strong patches of continuous spectrum around λ 3340 and λ 4550 were in reality only the most intense regions of a spectrum, reaching from the red to a point very near λ 2536 52. Thus the connection of λ 2536 52 with the visible continuous spectrum was not apparent, and their attention was not concentrated on the question here proposed. The distribution of intensity in this spectrum is in fact somewhat as in the figure, when heights above the base line roughly represent intensities. With reduced intensity (and in work of this kind, lack of intensity is always the difficulty) the portions *a b c* appear detached, and *c* may itself simulate the line 2536 52, particularly if the experimenter succumbs to the temptation to use a wide slit. There is a further complication due to the band 2540 to be presently discussed.



Van der Lingen and Wood (*loc cit*) used a silica bulb containing mercury, but exhausted of air, and examined the fluorescence excited by the aluminium spark at various vapour densities. In accordance with the earlier observations of Wood, they found an emission line at λ 2536 52 when the temperature and, consequently, the vapour density was low, but it faded out at higher temperatures. My own experience was similar. At low densities it is necessary to be very careful to avoid discharges in the exhausted bulb by electrostatic induction from the spark and its connecting wires, if the spectrum of the fluorescence is to be examined. I believe, however, that this was satisfactorily achieved, and that there is no doubt that the appearance of 2536 52 at low densities under the aluminium spark was genuine, thus confirming the conclusion of Van der Lingen and Wood

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* For references see a paper by Van der Lingen and Wood, 'Astrophysical J,' vol 54, p. 149 (1921).

The results of the present investigation will best be described by reference to Plate 8 The photographs II–V were obtained by means of a Hilger quartz spectrograph of medium size, giving a dispersion of 0 12 mm per Ångström in this region They are enlarged 8 times

II is a photograph of the fluorescent light of mercury vapour in an exhausted silica bulb under the aluminium spark The temperature was raised to the point when the green fluorescent light was confined to a few mm thickness of the vapour representing the stratum in which the effective radiation was absorbed The spectrograph was pointed in a direction at right angles to the incident light, and the exposure was about 50 hours The comparison spectrum was from a mercury vapour discharge tube It shows the resonance line 2536 52 $1S-1p_2$, and another series line 2534 77 $1p_3-3d$ These lines, one or both of which appear on all the photographs II to V, have been used to place them in register by means of the ink lines ruled on the mount In the central strip of II we see a continuous band ended abruptly to the left at wave length 2535 9, and shading off indefinitely to the right (longer wave-lengths) According to the view here taken, this is the continuous spectrum shown in photograph I The complete range of spectrum of the fluorescent light of the aluminium spark (not shown) shows nearly the same distribution of intensity as the figure already given with the characteristic feature of beginning near 2536 52 The comparison along the whole range of spectrum from this point is somewhat embarrassed by the unavoidable presence of aluminium lines due to stray light from the spark, and also probably to a little continuous spectrum from the same source, which seems to make the fluorescent spectrum relatively more intense in the visual region But, upon the whole, the comparison seems clearly to bear out the identity of the two spectra In particular, the characteristic broad maximum at about λ 3340, symmetrically situated between the mercury lines 3132 and 3650, appears in each

Accepting this identification, we have now to scrutinise closely the region of this continuous spectrum near the resonance line 2536 52 as shown in photograph II There are two dark lines or bands seen by reversal on the continuous background One of these is the reversal of the resonance line itself 2536 52 We should expect this since much of the light emerges through a layer of some thickness, and we know that 2536 52 appears as a strong absorption line of mercury vapour in its normal state If, therefore, this line is not excited to emission, we should expect it to appear in absorption, as observed.

The second dark line is at wave length 2540. Absorption by mercury vapour at this point has already been noted by Stark and Wendt,* though their reproduction does not show it so clearly as the present photograph should do, if successfully reproduced

This absorption band represents the reversal of the emission band known in the literature as 2539 or 2540

The other bright lines seen to the right in photograph II are due to stray light from the aluminium spark

There is a point in connection with this photograph requiring further discussion It refers to the last feature on the left. According to the interpretation adopted, this is merely a strip of continuous spectrum limited on the left by the end of this continuous spectrum at 2535 9, and on the right by the absorption line 2536 52 But, alternatively, it might be suggested that this feature is itself an emission line Though it is difficult absolutely to disprove this suggestion, yet there is nothing to favour it No line can be detected at this position in the exciting spark, nor has it ever been suggested that such a line forms part of the spectrum of mercury or fits in with its series relations

Photograph III shows the fluorescent spectrum of mercury vapour under the aluminium spark, the vapour being at lower density than in II Before taking it, the flame which kept the silica bulb hot was considerably lowered The green fluorescence then expanded from the wall near the spark to fill the whole bulb, and became fainter, until only just visible Under these circumstances the line 2536 52 and the band 2540, instead of being dark on a bright ground, are seen bright on a dark ground No other mercury line came out Aluminium lines are seen to the right as in II

IV shows much the same features as III, but in this case the excitation is by taking the induction coil discharge directly through somewhat dense mercury vapour, distilling up from a mercury surface The conditions are in fact the same as in I, but the exposure is adjusted to bring out the details near 2536 52, and is not strong enough to bring out the continuous background to the right of this line, which reaches over the whole spectrum, as in I The features brought out in IV are 2536 52, the band 2540, and the line 2534 77, all in emission

V is the absorption spectrum of mercury vapour, taken through a layer 6 cm in length The vapour was at atmospheric pressure, but it filled the vessel to the exclusion of air The source of light was a cadmium spark, and the strong line to the right is the cadmium line 2573 This is a repetition of one of R W Wood s early experiments.* It is introduced here to show that the continuous emission spectrum seen in I and II appears in absorption if the quantity of mercury vapour is large enough The sharp limit on the short wave length side was measured as 2535 5 in the absorption spectrum (V) and 2535 9 in the emission spectrum (II) and may be considered to be the same in each as nearly as it is possible to regard it as definite The exact limit has of course no meaning without fuller definition which would require a consideration of the intensity as a function of wave length for it is not to be supposed that the apparent discontinuity of intensity would survive a close enough examination The apparent position of the limit doubtless depends to some extent on intensity and length of photographic exposure

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* 'Phys. Zeit,' vol. 14, p. 567 (1913)

It may be objected that the absorption does not extend throughout the spectrum into the visual region as does the continuous emission shown in I We must remember however that a feeble absorption is not so easily brought into evidence as a feeble emission The former can only become apparent if we have a satisfactorily uniform bright background on which to observe it and even then it will not be very conspicuous unless we can bring up the absorption to at least 20 per cent of the incident light In the case of emission there is no limitation of this kind Long exposure can compensate for feeble intensity

In some of Wood s absorption experiments with dense vapour the absorption is as a matter of fact brought to as much as 420 Ångströms towards the visual region to wave length 2950 Photograph I it must be admitted would lead us to expect that absorption would be more conspicuous in the region near the mercury line 3341 than it is observed to be if the absorption were an exact counterpart of the emission

Another point to be noticed is that the emission of 2536 52 and 2540 shown in III and IV do not agree very closely in position with the absorption or reversal of these features shown in II Indeed if we confine ourselves for the moment to II alone the absorption line which has been taken to represent the reversal of 2536 52 will be seen to be decidedly displaced to the less refrangible side of this line as seen in the comparison spectrum This may be due to a slight development of the phenomenon seen in V Again the emission of 2540 in III and IV may be apparently somewhat displaced to the left by superposition on a bright background shading off to the right, as in II In any case, these are residual phenomena which may be left for further investigation

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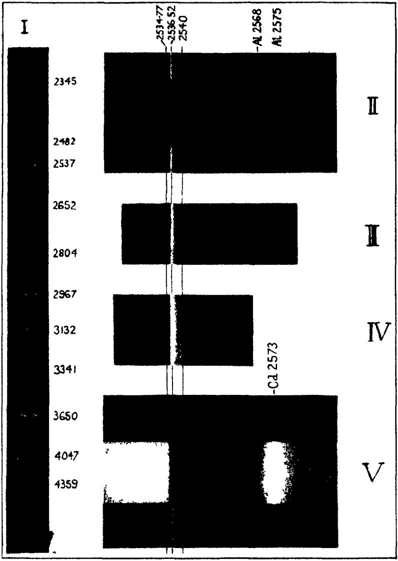
* Phil Mag vol 18, p. 240 (1909)


I
2534·77
2536 52
2540
Al 2568
Al 2575
2345
2482
2537
2652
2804
2967
3132
3341
3650
4047
4359
II
III
IV
Cd 2573
V

Summary

This paper discusses the various features of the mercury spectrum in the neighbourhood of the resonance line 2536 52 $1S-1p_2$, and in particular the relation of this line to the continuous spectrum extending over the whole region from near this point to the green and even into the red

The continuous spectrum can be produced without the resonance line by fluorescent excitation with the aluminium spark as originally observed by Wood Under these conditions it is found that the continuous spectrum ends at 2535 9 thus about 0 6 Ångström on the short wave length side of the resonance line In this case the resonance line appears dark on the continuous background The band at 2540 also appears sharply reversed on this background

The same continuous spectrum can be obtained in absorption In this case the measured limit was 2535 5 thus 1 Angstrom on the short wave length side of the resonance line But with a diminished quantity of absorbing vapour the limit would probably be at the same position as for the emission spectrum

By lowering the density of the vapour the spectrum in this region with aluminium spark excitation is completely reversed the resonance line 2536 52 and the band 2540 now appearing bright on a comparatively dark back ground The same effect is obtained by electric discharge in fairly dense vapour if the exposure is not too heavy Reproductions of the various spectra accompany the paper

DESCRIPTION OF PLATE 8

I Spectrum of induction coil discharge in fairly dense mercury vapour Note the continuous spectrum from near the line 2536 52 (marked 2537)

II Enlarged spectrum of fairly dense mercury vapour excited to fluorescence by aluminium spark Note continuous spectrum from 2535 5 on 2536 52 and the band 2540 appear dark upon it as a bright background

III The same with lowered density of mercury vapour The line 2536 52 and the band 2540 now appear in emission

IV Dense mercury vapour under electric discharge of induction coil Same features as in III.

V Absorption spectrum of 6 cm of mercury vapour at 760 mm pressure Shows the same continuous spectrum as II in absorption. Cadmium spark used as source This is the origin of the strong line 2573

The Alkali Perchlorates and a New Principle concerning the Measurement of Space-lattice Cells

By A E H TUTTON, M A , D Sc , F R S

(Received April 29, 1926)

The perchlorates of potassium and ammonium, $KClO_4$ and NH_4ClO_4, were investigated crystallographically first by Mitscherlich[*] in the year 1832, then more extensively by Groth[†] in 1868, and later still more fully, in 1907, by T V Barker[‡] in Oxford, who also included the perchlorates of rubidium and cæsium, $RbClO_4$ and $CsClO_4$ in his investigations The scope of all this work, however, only extended to the morphological characters, no optical properties or constants having been dealt with, except as regards some very roughly approximate data given by Groth for the potassium and ammonium salts, which, moreover, in the case of the potassium salt, has proved to be erroneous The optical investigation of these salts is rendered exceptionally difficult by the fact that only very small crystals can be obtained , especially is this true of the three metallic salts, the largest obtainable crystals rarely reaching the size of a small pin's head and the most perfectly developed ones being only half that size The author has long considered it a matter of special importance that the optics of these alkali perchlorates should, if possible, be thoroughly worked out, and recent developments of the X-ray study of crystals, connecting structure with refraction, have rendered this all the more desirable Such an investigation has, therefore, been attempted, and happily with complete success, although it has proved the most difficult one ever undertaken by the author For reasons which will be clear from what follows, a complete remeasurement of the crystals of all four salts has also been made, with most satisfactory confirmation of the results of Barker, and extension of them to further important angles and a new " setting " The densities of the crystals as determined by Barker required no revision, as they were obtained, obviously with particular care, by the author's mode of carrying out the Retgers immersion method, using a mixture of methylene iodide and toluene as the immersion liquid

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[*] E Mitscherlich, 'Pogg Ann. d Phys ,' vol 25, pp 286, 300 (1832)

[†] P von Groth, 'Pogg Ann. d. Phys ,' vol. 133, p. 213 (1868) , 'Chem Kryst ,' vol 2, pp. 167, 173 (1908).

[‡] T V Barker, 'Zeitschr für Kryst ,' vol 43, p 529 (1907), and vol 45, p 17 (1908)

Three outstanding results arose from the work of Barker Firstly it was shown that potassium rubidium and cæsium perchlorates form a eutropically isomorphous series of orthorhombic salts resembling in this respect the sulphates and selenates of these same three metals studied by the author and the alkali permanganates studied by Muthmann * Secondly ammonium perchlorate proved to be closely isostructural with rubidium perchlorate just as the sulphates and selenates of the same two bases had been found to be by the author Thirdly Barker showed that these perchlorates and the corresponding permanganates are isomorphous with the barytes group of orthorhombic minerals barytes $BaSO_4$ celestine $SrSO_4$ and anglesite $PbSO_4$ and that the morphological constants (unit cell dimensions as indicated relatively by the topic axial ratios) in the cases of barytes and potassium perchlorate and permanganate are so close that overgrowths and parallel growths of the two latter salts are readily formed from their solutions on the crystals of barytes

The following table will render these results of Barker clear the figures are compiled from his 1908 paper and a more recent one and include the three principal angles the molecular volume and the topic axial ratios for both the perchlorates and permanganates and the barytes group —

	m m	q	c r	Mol vol	χ	ψ	ω	ξ
$KClO_4$	76 1	52 1	39 19	54 91	3 7360	4 7878	6 1307	3 0365
$RbClO_4$	77 5	—	38 57	61 33	3 9244	4 9264	6 3447	3 1492
$CsClO_4$	78 31	52 23	38 27	70 05	4 1625	5 0929	6 6086	3 2888
$AmClO_4$	76 50	52 1	38 55	60 19	3 8959	4 9117	6 2909	3 1346
$TlClO_4$	77 10	—	38 57	62 66	3 9964	5 0093	6 2606	3 2040
$KMnO_4$	77 8	52 24	39 9	58 53	3 8555	4 8360	6 27 9	3 0924
$RbMnO_4$	79 28	53 7	38 48	63 23	4 0362	4 8565	6 4704	3 1574
$CsMnO_4$	81 56	53 53	38 17	70 04	4 2551	4 9005	6 7161	3 2450
$AmMnO_4$	78 28	52 47	38 53	62 13	3 9757	4 8698	6 4126	3 1433
Barytes	78 23	—	—	52 0	3 6509	4 7899	5 94 2	3 0113
Celestite	75 58	—	—	46 6	3 5349	4 5931	5 7649	2 8980
Anglesite	76 17			48 2	3 5743	4 5520	5 8394	2 8938

Now it is highly interesting in this connection that the structure of barytes has recently been worked out independently by X ray analysis by three different sets of investigators namely by Rinne Hentschel and Schiebold † by Wyckoff and Merwin ‡ and by James and Wood § and all agree that the space group

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* W Muthmann *idem* vol 22 p 527 (1894)

† Zeitschr für Kryst vol 64 p 164 (1925)

‡ *Idem* vol 64 p 453 (1925) and Amer Journ Sci vol 9 p 286 (1925)

§ Roy Soc. Proc A vol 109 p 598 (1925)

is the orthorhombic holohedral (class 8 di digonal equatorial) one V_h^{16} of Schoenflies The absolute dimensions of the unit cell which is the rectangular parallelepipedal one of the simple orthorhombic space lattice, No 10, and contains four molecules of $BaSO_4$ have been obtained in Ångström units, the mean of the closely agreeing values being $a = 8\ 87$, $b = 5\ 44$, and $c = 7\ 15$ Moreover, as large transparent and very perfect crystals of barytes are available particularly suitable for X ray reflection intensity determinations, the arrangement and positions of the atoms in the structure have also been determined by James and Wood The SO_4 group appears to be of tetrahedral character, with the sulphur atom at the centre of the tetrahedron, to which the oxygen atoms are strongly attracted, both the barium atoms and the sulphur atoms lie in the symmetry planes parallel to (010) the axial plane *ac* Precisely analogous results were obtained for celestine $SrSO_4$ and anglesite, $PbSO_4$ good crystals being also available but the cell dimensions are, of course very slightly different For celestine $a = 8\ 36$ Å, $b = 5\ 36$ Å, and $c = 6\ 84$ Å For anglesite the values afforded were $a = 8\ 45$ Å, $b = 5\ 38$ Å, and $c = 6\ 93$ Å

Further James and Wood carried out a number of observations with potassium perchlorate $KClO_4$, and all agreed in indicating that its structure is essentially similar to that of barytes, celestine and anglesite and the main spacings, corresponding to the dimensions of the cell edges were found to be $a = 8\ 84$ Å, $b = 5\ 68$ Å and $c = 7\ 22$ Å But the technical difficulties of making accurate intensity measurements with crystals so small as the largest obtainable of any of the alkali metal perchlorates are insuperable

Now it is an important fact not hitherto noticed, that in the cases of strictly analogous isomorphous structures, such as barytes and the perchlorates we have in the crystallographic constants known as topic axial ratios" the means of calculating the absolute cell edge dimensions, given one thoroughly measured (by X rays) member of the series, obtainable in large perfect crystals, such as barytes in the case of the isomorphous series under consideration And it will be shown as one of the results of the present investigation that, for instance, the absolute lengths of the edges of the unit cells of potassium perchlorate, as thus calculated from the topic axes and the knowledge of the edge lengths of the barytes cells, are within one to four units in the second place of decimals of the values of James and Wood just quoted as obtained by X-ray analysis, namely, $a = 8\ 85$ Å, $b = 5\ 67$ Å, and $c = 7\ 26$ Å With the confidence given by this remarkably good agreement, the absolute dimensions of the cells of the perchlorates of rubidium, cæsium and ammonium have also been calculated, from the author's topic axial ratios, and will be given in the course of this communication The author's topic axial ratios thus used are quite different from those of Barker, being calculated for the rectangular orthorhombic cell indicated by the X-ray work of all three sets of investigators referred to, which not only differs in not being that corresponding to the rhombic prismatic lattice assumed by Barker, but also has an axis *a* of double the length, this being clearly indicated to be the "correct setting" by the X-ray analysis

Before giving the detailed results of this investigation it should be mentioned that the method of Groth and Barker was strictly followed, for the preparation of the perchlorates of rubidium and cæsium, by decomposing the sulphates of these alkali metals (in solution) with barium perchlorate solution The latter salt was specially prepared in pure state for the author by Messrs Hopkin and Williams

The difficulty, as regards the optical part of the investigation, of the very small size of the crystals obtainable of the three metallic perchlorates was overcome by the use of natural plates and prisms, which was rendered possible by the two facts that the crystals are orthorhombic and that the faces of the forms *c* {001}, *m* {110} and *r* {102} (Groth indices) were extraordinarily perfect on an adequate number of crystals, affording perfect, single, and very brilliant images of the goniometer signal-slit For a pair of *m*-faces (with intervening *b*-face strip), and a pair of *r*-faces (with intervening *a*-strip), each form a prism affording two of the refractive indices directly and together all three refractive indices, with one in duplicate, and, in spite of the very minute size, with the author's arrangement for powerful monochromatic light the refracted images of the signal were often quite brilliant and always trustworthy The somewhat larger crystals of the ammonium salt were partly investigated in the same way, and partly by grinding 60° prisms with the cutting-and-grinding goniometer, the results being identical For the optic axial angle determinations with the metallic salts crystals with the pairs of parallel *c*-faces best developed were used, their normal being one of the bisectrices, and the optic axial angle was measured by immersing the crystal in a liquid of the same mean refractive index Refined spirits of turpentine, toluene, and para-xylene, the latter most kindly supplied by Sir William Pope and Mr Stoakley of the Cambridge University Laboratory, proved very suitable liquids, their refractive indices were determined with great care, with a small hollow prism on the same goniometer-refractometer (Fuess, No 1A) as was used for the crystal prisms In the case of the ammonium salt, sections perpendicular to the two bisectrices were ground as usual, the crystals being just large enough to permit of this being done

As regards the "correct setting" of the crystals for the descriptive purposes, now so very important a matter, that indicated unanimously by all the three parties of X-ray investigators, is adopted in this memoir It is that of a rectangular rhombic parallelepipedal cell, the edges corresponding to the crystallographic axes *a*, *b*, and *c*, and with the axis *a* twice as long as in the hitherto accepted Mitscherlich-Groth-Barker setting The indices (h, k, l) of the latter become now ($2h$, k, l) in consequence Moreover, the topic axial ratios given in the descriptions are those corresponding to the edges of this rectangular cell, and represent the relative lengths of the edges Those corresponding to the Barker rhombic prismatic cell are also given, however, as are the Groth indices in the descriptions, for convenience of reference The Groth lettering of the faces is retained

Potassium Perchlorate $KClO_4$

A particularly pure preparation of the salt was supplied by Messrs Hopkin and Williams, and several times recrystallised The crystals eventually obtained for the research after many attempts with less success, were always small, even as understood by the crystallographer for goniometrical purposes, rarely attaining the size of an ordinary pin's head, but they were remarkably perfect, the faces of all the selected ones being truly plane, affording exceptionally sharp single and brilliant images of the Websky signal-slit The goniometrical measurements were consequently unusually concordant

Crystal-System, Class, and Space-Group —Orthorhombic, holohedral class 8, rhombic bipyramidal, di-digonal equatorial, space-group of Schoenflies V_h^{16}

Forms Observed —*c* {001}, *m* {210} the (110) of the old setting, *r* {101} the former {102}, these three always well developed, *b* {010}, *a* {100}, *q* {011}, and *o* {211} the former {111}

Habit —The most extensively developed of all the forms were always the basal pinakoid *c* {001}, the faces of which were usually the larger, and the rhombic prism *m* {210}, these two forms determining the habit, which was thus thickly tabular parallel *c* {001}, the prism being usually short vertically, as indicated in fig 1, which is very typical of the majority of the crystals obtained

The next best developed form was the primary macrodomal prism *r* {101}, the faces of which were somewhat squat isosceles triangles, with base parallel to axis *b*. The faces of the macropinakoid *a* {100} were not always present, and were never larger than narrow strips joining the apices of the triangular *r* faces But the faces of the brachypinakoid *b* {010} were often quite well

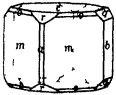


FIG 1 —A Typical Crystal of Potassium Perchlorate

developed blunting the sharper edges of the primary prism at the ends of the *b* axis The faces of the primary brachydomal prism *q* {011} and of the rhombic bipyramid *o* {211} were not always developed and the latter were particularly rare and always relatively very small the former form was however not infrequently represented by good little facets sometimes strips and sometimes triangles blunting the edges between *b* {010} and *c* {001}

Numerous attempts to obtain good larger crystals were never successful Whenever the size exceeded that of a pin s head by permitting prolonged evaporation at the ordinary temperature or crystallising from large quantities of saturated solution the perfection was destroyed the crystals being thus untrustworthy for accurate measurement or determination of optical constants

Axial Ratio *a* *b* *c* 1 5626 (or 0 7813 for old setting) 1 1 2807 The axial ratio given by Groth was 0 7817 1 1 2792 and by Barker as 0 7815 1 1 2805 The author s values are remarkably close to those of Barker and agree also quite well with those of Groth

Crystal Angles —A table of the angular measurements with ten very perfect crystals follows

Cleavage —Perfect parallel *c* {001} and *m* {210} common to the whole series

Density —2 524 mean of the values of Muthmann and of Barker and adopted by the latter

Molecular Volume Barker s value $V = 54\ 91$ is adopted

Topic Axial Ratios The calculated values are given below using Barker s V and the author s crystallographic axial ratios both for the Barker Groth setting and for the true setting indicated by X rays For the former the formulæ used were $\chi = \sqrt[3]{\frac{2Va^2}{c}}$ $\psi = \sqrt[3]{\frac{2V}{ac}}$, $\omega = \sqrt[3]{\frac{2Vc^2}{a}}$ corresponding

Morphological Angles of Potassium Perchlorate

Angle			No of measurements	Limits	Mean observed	Calculated.	Difference	Barker's values
	X ray Setting	Old Setting		° ′ ° ′	° ′	° ′	′	° ′
am	= (100) (210)	or (100) (110)	18	37 56–38 6	38 0	38 0	0	—
mb	= (210) (010)	,, (110) (010)	40	51 53–52 3	52 0	—*	—	51 59
mm	= (210) $(\bar{2}10)$	,, (110) $(\bar{1}10)$	20	75 59–76 4	76 1	76 0	1	76 1
ar	= (100) (101)	,, (100) (102)	22	50 36–50 42	50 39	50 39	0	—
rc	= (101) (001)	,, (102) (001)	36	39 15–39 26	39 21	—*	—	39 19
rr	= (101) $(10\bar{1})$	,, (102) $(10\bar{2})$	20	101 13–101 22	101 19	101 18	1	—
bq	= (010) (011)	,, (010) (011)	24	37 53–38 7	38 0	37 59	1	37 59
qc	= (011) (001)	,, (011) (001)	24	51 53–52 3	52 0	52 1	1	52 1
ao	= (100) (211)	,, (100) (111)	4	44 43–44 50	44 46	44 45	1	—
oq	= (211) : (011)	,, (111) (011)	6	45 10–45 19	45 14	45 15	1	-
bo	= (010) (211)	,, (010) (111)	2	56 17–56 23	56 18	56 20	2	
oo	= (211) $(2\bar{1}1)$	,, (111) $(1\bar{1}1)$	1	-	67 24	67 20	4	—
co	= (001) (211)	,, (001) (111)	10	64 16–64 29	64 21	64 20	1	64 19
om	= (211) (210)	,, (111) (110)	10	25 29–25 42	25 37	25 40	3	—
mr	= (210) (101)	,, (110) (102)	4	59 59–60 5	60 2	60 1	1	—
rm	= (101) $(\bar{2}10)$	,, (102) $(\bar{1}10)$	4	119 55–120 1	119 58	119 59	1	—
mo	= (210) : $(2\bar{1}1)$	,, (110) $(1\bar{1}1)$	—	—	—	77 24	—	—
om	= $(2\bar{1}1)$ $(\bar{2}10)$	,, $(1\bar{1}1)$ $(\bar{1}10)$	-	—	—	102 36	—	—

to the rhombic prismatic lattice No. 8 For the latter the formulæ employed were $\chi = \sqrt[3]{\frac{Va^2}{c}}$, $\psi = \sqrt[3]{\frac{V}{ac}}$, $\omega = \sqrt[3]{\frac{c^2V}{a}}$ corresponding to the rectangular orthorhombic lattice No 10, the axial ratio a/b used for this setting also had the true double value 1 5626

For the true setting by X-rays $\chi = 4\ 7130$, $\psi = 3\ 0161$, $\omega = 3\ 8628$

For the Groth-Barker setting $\chi = 3\ 7408$, $\psi = 4\ 7878$, $\omega = 6\ 1318$ Barker's values were 3 7360, 4 7878, and 6 1307, the agreement being thus very satisfactory

Optical Characters and Optic Axial Angle—The only data hitherto given are the following, by Groth ('Chem Kryst,' vol 2, p 168) —Double refraction positive, feeble, plane of optic axes *c* {001}, first median line axis *b*, 2V = 70°–80°, one axis visible through *m* {110}

A very thorough investigation, fully confirmed by the refractive index determinations, has shown that the plane of the optic axes is not *c* {001} but *a* {100}, the second median line being the axis *c*, and not the axis *a*, as it would be if the optic axial plane were *c* {001}. The first median line is the axis *b* as correctly given by Groth When a tabular crystal parallel *c* {001} is immersed (its plane being vertical and axis *b* horizontal and its normal parallel to the axis of the polariscope) in turpentine the refractive index of which is practically identical with the mean crystal index the optic figure is not only seen at its obtuse angle but on rotation of the crystal for a complete circle the optic brushes are seen at both the obtuse and the acute angles of the optic axis and duplicate determinations of each angle can readily be obtained Owing to the feebleness of the positive double refraction and to the fact that the largest and thickest obtainable crystal tabular parallel *c* {001} is scarcely half a millimetre thick the brushes are somewhat diffuse but in the cases of three excellent little crystals employed for the purpose gave the following results for the value of the true angle $2V_a$ between the optic axes The approximate value mentioned by Groth will be seen to be much too large

Optic Axial Angle of Potassium Perchlorate

Light *	Crystal 1	Crystal 2	Crystal 3	Mean 2V
				°
Li	50 18	50 21	50 14	50 18
C	50 15	50 18	50 11	50 15
Na	49 58	49 50	49 37	49 48
Tl	49 39	49 32	49 14	49 28
Cd	49 10	49 21	48 55	49 9
F	48 42	49 2	48 30	48 48

* Li means red light supplied by the author s monochromator of the wave length of the lithium red line C that corresponding to the red Hα hydrogen line Na that of the wave length of the sodium D lines Tl that of the green thallium line Cd that of the cadmium green line F that of hydrogen greenish blue Hβ and G that of the violet light of Hγ of hydrogen all by use of the monochromator

Refractive Indices Four perfect little natural prisms each formed by two *m* faces at their 76° angle (the refracting edge being a *b*-face strip) and four others formed similarly by two *r* faces at their 78° angle afforded an excellent series of refractive index determinations in spite of their extremely small size The former (*m* prisms) each yielded the refractive indices α and γ corresponding to vibrations parallel to the axes *c* (parallel prism edge) and *b* respectively and the latter (*r* prisms) each afforded γ and β the vibrations being parallel to axes *b* (edge) and *a* respectively The accompanying table embodies the mean results

Refractive Indices of Potassium Perchlorate

Light	α Vibrations parallel axis c 2 M L	β Vibrations parallel axis a	γ Vibrations parallel axis b 1 M L
Li	1.4708	1.4714	1.4746
C	1.4712	1.4718	1.4760
Na	1.4731	1.4737	1.4769
Tl	1.4749	1.4755	1.4787
Cd	1.4761	1.4766	1.4799
F	1.4774	1.4779	1.4812
G	1.4810	1.4815	1.4848

Mean Refractive Index $\frac{\alpha+\beta+\gamma}{3}$ for sodium light 1.4746

Double Refraction Positive and weak $\gamma - \alpha$ for sodium light 0.0038

General Formula for Intermediate Index β — The refractive index β corrected to a vacuum the correction being $+0.0004$ is expressed by the following formula

$$\beta = 1.4616 + \frac{550\,560}{\lambda^2} - \frac{4\,049\,400\,000\,000}{\lambda^4} + $$

The α indices are also reproduced by this formula if the constant 1.4616 be decreased by 0.0006 and the γ indices if it be increased by 0.0032

Molecular Optical Constants The Specific and Molecular Refractions and Dispersions calculated by the Lorenz formula are

		Specific			Molecular		
		α	β	γ	α	β	γ
Refraction	For C Light	0.1108	0.1109	0.1115	15.35	15.37	15.46
	G Light	0.1128	0.1129	0.1135	15.63	15.64	15.73
	Dispersion	0.0020	0.0020	0.0020	0.28	0.27	0.27

The Molecular Refractions for C light calculated by the Gladstone formula are $\alpha = 25.88$ $\beta = 25.91$ $\gamma = 26.08$ Mean Molecular Refraction (Gladstone) $\frac{\alpha+\beta+\gamma}{3}$, for C light, 25.96

Rubidium Perchlorate, $RbClO_4$

The crystals of this salt were the smallest of all four alkali perchlorates and afforded greatest difficulty in the optical investigation But they were remarkably perfect as regards planeness and brilliancy of their faces enabling excellent goniometrical measurements to be carried out

Crystal System, Class and Space-Group —Same as for potassium perchlorate

Forms Observed — c {001} *m* {210} the {110} of the old setting *o* {211} the {111} of old setting these three well developed *b* {010}, and *r* {101} the former {102} both fairly developed *a* {100} rare and minute and not observed by Barker

Habit -Great diversity of habit was exhibited by the crystals of the numerous crops prepared some of which were quite peculiar to this salt of the series The relatively large development of the faces of the rhombic bipyramid *o* {211 was largely responsible and the fact that the faces of this form were alternately large and small In the most evenly developed type found in comparatively few crops the crystals are of thick tabular character resembling fig 2 with the *o* {211} and *m* {210} faces both well developed *m* somewhat predominatingly and c {001} as the table faces But numerous other crops showed crystals like fig 3 in which the *m* and *o*-faces are developed alternately the larger so that the *m* faces were rarely opposite to one another and it was only after examining a very large number of crystals of different crops that specimens like fig 2 could be found suitable for use of a pair of acutely inclined *m* faces as a prism for refractive index determinations The [c o m] zones were so prominently developed in other crops especially the *o* faces as to produce house roof shaped blocks like fig 4 Still another type is shown in fig 5 which is characterised by vertically long *m* {210} faces capped by roof like pairs of *o* {211} faces the latter alternately arranged at the upper and lower ends of the vertical axis as in hemimorphic crystals This type

FIG 2

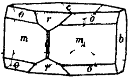
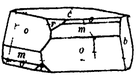


FIG 3



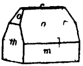


FIG 4

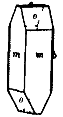


FIG 5

Typical Crystals of Rubidium Perchlorate was only found in one crop, one of the last prepared, and happily solved the search for *m*-faced prisms suitable for refractive index measurements, affording two brilliant spectra, corresponding to the α and γ indices, in spite of their minute size.

Good *b* {010} faces were the rule, more or less strip-like, but *a* {100} was very rare, and only found twice, and then only measurable in the [*a r c*] zone. The *q* {011} faces were never observed developed. The faces of *r* {101} were relatively very small, smaller than in the other salts of the series.

Axial Ratio. *a* : *b* : *c* = 1·5928 : 1 : 1·2884. Or 0·7964 : 1 : 1·2884 for the old setting. Barker obtained 0·7966 : 1 : 1·2879, the agreement being thus excellent.

Crystal Angles.—A table of the measured angles follows.

Angles of Rubidium Perchlorate

Angle	No of measurements	Limits	Mean observed	Calculated	Difference	Barker's values
X ray Setting Old Setting		° ′	°	° ′	′	° ′
am = (100) : (210) or (100) (110)	—	—	—	38 32		—
mb = (210) (010) ,, (110) (010)	48	51 25–51 32	51 28	—*	—	51 27
mm = (210) $(\bar{2}10)$,, (110) : $(1\bar{1}0)$	24	76 59–77 8	77 4	77 4	0	77 5
ar = (100) (101) , (100) : (102)	2	51 0–51 2	51 1	51 3	2	—
rc = (101) (001) ,, (102) (001)	34	38 49–39 5	38 57	—*	—	38 57
rr = (101) : $(10\bar{1})$ (102) $(10\bar{2})$	16	101 57–102 12	102 5	102 6	1	—
bq = (010) : (011) (010) (011)	—	—	—	37 49	-	—
qc = (011) (001) (011) (001)	-	-	-	52 11	—	—
ao = (100) (211) ,, (100) (111)	--	—	—	45 14	--	—
oq = (211) : (011) ,, (111) (011)	-	-	—	44 46	—	—
bo = (010) (211) , (010) (111)	24	55 50–55 55	55 52	55 53	1	—
oo = (211) $(2\bar{1}1)$, (111) $(1\bar{1}1)$	10	68 14–68 18	68 15	68 14	1	—
co = (001) : (211) ,, (001) (111)	46	64 8–64 18	64 13	64 11	2	64 11
om = (211) (210) ,, (111) (110)	45	25 41–25 54	25 48	25 49	1	25 49
mr = (210) (101) ,, (110) (102)	2	60 30–60 34	60 32	60 33	1	60 33
rm = (101) $(\bar{2}10)$,, (102) $(\bar{1}10)$	2	119 26–119 30	119 28	119 27	1	—
mo = (210) : $(2\bar{1}1)$,, (110) $(1\bar{1}1)$	5	78 23–78 25	78 24	78 23	1	—
om = (211) $(\bar{2}10)$,, $(1\bar{1}1)$ $(\bar{1}10)$	5	101 35–101 37	101 36	101 37	1	—
ro = (101) (211) ,, (102) : (111)	4	38 37–38 44	38 40	38 37	3	—

Cleavage.—Parallel *c* {001} and *m* {210}, both very good.

Density.—3·014 (Barker).

Molecular Volume.—V = 61·33 (Barker).

Topic Axial Ratios.—For true setting, by X-rays, $\chi = 4.9429$, $\psi = 3.1033$, $\omega = 3.9982$. For old setting (Groth-Barker), $\chi = 3.9232$, $\psi = 4.9262$, $\omega = 6.3469$.

Barker's values were 3.9244, 4.9264, 6.3447, the agreement thus being good.

Optical Characters and Optic Axial Angle. Closely resembling those of potassium perchlorate. A crystal tabular parallel $c\{001\}$ shows the optic figure symmetrical to the centre, but the optic axes are just outside the widest polariscopical field, the normal to the plate, axis c, being the second median line. Axis b is the first median line, and the plane of the optic axes is thus $a\{100\}$. The double refraction is feeble and positive. In turpentine, of like refractive index to the crystal, the optic axial brushes are well seen although somewhat diffuse and both the acute and obtuse angles between the optic axes can be readily measured. The results with three such plates, the thickest tables parallel $c\{001\}$ obtainable, are as follows:—

Optic Axial Angle of Rubidium Perchlorate

Light	Crystal 1	Crystal 2	Crystal 3	Mean $2V_a$
	° ′	° ′	° ′	° ′
Li	55 27	55 22	54 51	55 13
C	55 25	55 21	54 49	55 12
Na	55 18	55 14	54 40	55 4
Tl	55 12	55 8	54 25	54 55
Cd	55 2	55 0	54 10	54 44
F	54 50	54 50	54 0	54 33

Refractive Indices. Eight natural prisms formed by perfect little faces were found, after much searching among many crops of crystals, suitable for refractive index determinations. Three were formed by m faces with b-face strip modifying the refracting edge and afforded α and γ, one was formed by a pair of r-faces, and yielded β and γ; two were formed by o faces with c-face as strip edge between them and afforded the minimum index α, and two others were also formed by o faces, but with a b-face as strip edge in each case, and afforded the maximum index γ. The following are the mean results of the very concordant individual ones.

Refractive Indices of Rubidium Perchlorate

Light	α 2 M L Vibrations parallel axis c	β Vibrations parallel axis a	γ 1 M L Vibrations parallel axis b
Li	1 4671	1 4681	1 4712
C	1 4674	1 4684	1 4715
Na	1 4692	1 4701	1 4731
Tl	1 4709	1 4719	1 4750
Cd	1 4720	1 4730	1 4761
F	1 4732	1 4742	1 4774
C	1 4767	1 4777	1 4809

Mean Refractive Index for sodium light, $\frac{\alpha + \beta + \gamma}{3} = 1\ 4708$

Double Refraction $\mathrm{Na}_{\gamma\ \alpha} = 0\ 0039$

General Formula for β (*in vacuo*) —

$$\beta = 1\ 4610 + \frac{360\ 771}{\lambda^2} - \frac{1\ 074\ 400\ 000\ 000}{\lambda^4} + $$

The formula also serves for α if the constant 1 4610 be diminished by 0 0010, and for γ if it be increased by 0 0031

Molecular Optical Constants —

		Specific			Molecular		
		α	β	γ	α	β	γ
Lorenz Refraction	For C Light	0 0921	0 0923	0 0928	17 03	17 06	17 16
	G Light	0 0937	0 0939	0 0944	17 32	17 35	17 45
,, Dispersion		0 0016	0 0016	0 0016	0 29	0 29	0 29

Gladstone Molecular Refraction for C Light $\begin{cases} \alpha = 28\ 67 \quad \beta = 28\ 73 \quad \gamma = 28\ 92 \\ \text{Mean, } \frac{\alpha + \beta + \gamma}{3} = 28\ 77 \end{cases}$

Cæsium Perchlorate $\mathrm{CsClO_4}$

The crystals obtained of this salt were exceedingly small, although somewhat larger than those of the rubidium salt but they were very perfect

Crystal System, Class, and Space Group —Same as for potassium and rubidium perchlorates

Forms Observed—*c* {001}, *m* {210} the (110) of the old setting always predominating, *b* {010}, *r* {101} the (102) of old setting, and *o* {211}, the former {111}, less prominent, *a* {100} and *q* {011} only occasionally developed

Habit—The crystals were either tabular parallel the basal pinakoid *c* {001}, as drawn in fig 6, or parallelepipedal blocks formed by *c* and *m* faces like fig 7 The brachypinakoid *b* {010} was usually present, and often one of its two faces was much more largely developed than the other The macropinakoid *a* {100} was relatively rare and exceedingly small it was not observed by

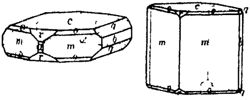


FIG 6 FIG 7

Typical Crystals of Cæsium Perchlorate

Barker The rhombic bipyramid *o* {211} was ubiquitous generally occurring as strip faces modifying the edges between the *c* and *m*-faces The faces of the primary macrodomal prism *r* {101} were generally relatively small, often only like points, but in several of the crystals measured were proportionally larger, and pairs of them on three such crystals served as excellent prisms for the determination of refractive indices The primary brachydomal prism *q* {011} was but rarely developed, and excessively small as a rule when present, but exceptionally good faces of this form were present on several of the measured crystals

Axial Ratio — *a* *b* *c* = 1 6340 1 1 2970 Or 0 8170 1 1 2970 for the old (Groth Barker) setting Barker's values were 0 8173 1 1 2976, the agreement being thus excellent

Crystal Angles —As given in the accompanying table (p 476)

Cleavage —Parallel *c* {001} and *m* {210}, perfect

Density —3 327 (Barker, 1907 paper, p 534)

Molecular Volume —69 84 in Barker's 1907 paper, p 535, but 70 05 in the 1908 paper this later value was also used in subsequent publications by Barker, so is adopted here in calculating the topic axial ratios

Topic Axial Ratios —For true setting by X-rays, $\chi = 5\ 2440$, $\psi = 3\ 2093$, $\omega = 4\ 1625$ For old setting (Barker), $\chi = 4\ 1621$, $\psi = 5\ 0944$, $\omega = 6\ 6074$

Barker's numbers (1908 memoir) were 4 1625, 5 0929, 6 6086, with which the above agree well

Optical Characters and Optic Axial Angle —Cæsium perchlorate differs optically from potassium and rubidium perchlorates in exhibiting negative double refraction While the plane of the optic axes is still *a* {100}, and the crystal-axes *b* and *c* are still the two median lines, vibrations parallel to

Angles of Cæsium Perchlorate

Angle	No of measurements	Limits	Mean observed	Calculated	Difference	Barker's values
X ray Setting Old Setting						
am = (100) (210) or (100) (110)	4	39 9– 39 20	39 14	39 15	1	—
mb (210) (010) (110) (010)	30	50 41 50 51	50 45	50 45	0	—
mm = (210) (2̄10) (110) (1̄10)	18	78 28 78 33	78 30	—*	—	78 31
mm = (210) (2̄10) (110) (1̄10)	16	101 28–101 32	101 30	101 30	0	—
ar = (100) (101) (100) (102)				51 34		
r = (101) (001) (102) (001)	37	38 18– 38 33	38 26	*		38 27
rr (101) (10̄1) (102) (10̄2)	16	103 4 103 20	103 10	103 8	2	
bq (010) (011) (010) (011)	7	37 29 37 40	37 35	37 38	3	—
qc = (011) (001) (011) (001)	7	52 20 52 30	52 24	52 22	2	52 23
ao = (100) (211) (100) (111)				45 54		
oq = (211) (011) (111) (011)				44 6	—	—
bo (010) (211) (010) (111)	2	55 16 55 22	55 19	55 21	2	
oo = (211) (21̄1) (111) (11̄1)	1		69 22	69 18	4	—
co (001) (211) (001) (111)	1	63 54 64 10	64 0	64 0	0	64 0
os (211) (210) (111) (110)	51	25 50– 26 10	26 0	26 0	0	26 0
mr = (210) (101) (110) (102)	2	61 10 61 12	61 11	61 13	2	61 13
rm = (101) (2̄10) (102) (1̄10)	2	118 47 118 50	118 48	118 47	1	
mo = (210) (21̄1) (110) (11̄1)	3	79 44– 79 45	79 44	79 41	3	—
om = (21̄1) (2̄10) (11̄1) (1̄10)	3	100 16 100 20	100 17	100 19	2	—

them afford the refractive indices γ and α respectively is now the acute bisectrix of the optic axial angle (first median line) and b the obtuse one the second median line Hence through a crystal tabular parallel to $c\{001\}$ the optic axial figure is visible with the optic axes themselves in the field even in air so that $2E$ as well as $2V_a$ are both measurable the latter in an immersion liquid of like refractive index The amount of dispersion of the optic axes for light of different wave lengths is so small that no clear difference could be accurately determined especially as even the thickest crystal with good c faces is still less than a small pin's head in size and the double refraction is very weak

Five crystals gave for $2V_a$ for all wave lengths of light and as the mean of immersions in turpentine toluene and para xylene the carefully determined refractive indices of the first of which were just lower, and those of the other two liquids slightly higher than the indices of the crystals, values ranging from 62° to 63½°, the exact mean value of all being 62° 30 Only the thickest and largest of the five crystals gave sharp axial brushes when the observations were conducted in air, and the mean value of 2E afforded was 101° 43′ for sodium light and all other wave-lengths from red Li light to F hydrogen light.

Refractive Indices.—Six natural prisms were used, three being formed by pairs of *m* faces (edge *a b* face strip) and three by *r* faces (edge containing a minute *a* face point). Each of the former yielded α and γ, and each of the latter β and γ. The accompanying table gives the mean results.

Refractive Indices of Cæsium Perchlorate

Light	α = 1st M. L. Vibrations parallel axis *a*	β. Vibrations parallel axis *c*	γ = 2nd M. L. Vibrations parallel axis *b*
Li	1.4730	1.4755	1.4782
C	1.4734	1.4760	1.4786
Na	1.4752	1.4788	1.4804
Tl	1.4771	1.4808	1.4824
Cd	1.4784	1.4821	1.4837
F	1.4807	1.4835	1.4862
G	1.4832	1.4860	1.4887

Mean Refractive Index for sodium light $\frac{\alpha+\beta+\gamma}{3} = 1.4781$

Double Refraction $Na_{\gamma-\alpha}$ = 0.0052

General Formula for β *in vacuo*

$$\beta = 1.4701 + \frac{307\,017}{\lambda^2} + \frac{278\,100\,000\,000}{\lambda^4} + \cdots$$

The formula also reproduces α if the constant 1.4701 be diminished by 0.0036, and γ if it be increased by 0.0016. The latter number being the smaller clearly indicates the negative sign of the double refraction.

Molecular Optical Constants

		Specific α	Specific β	Specific γ	Molecular α	Molecular β	Molecular γ
Lorenz Refraction constants	For C light	0.0844	0.0849	0.0852	19.61	19.73	19.79
	For G light	0.0859	0.0864	0.0867	19.95	20.08	20.15
Dispersion		0.0015	0.0015	0.0015	0.34	0.35	0.36

Gladstone Molecular Refraction for C light $\begin{cases} \alpha = 33.08 \quad \beta = 33.31 \quad \gamma = 33.43 \\ \text{Mean } \frac{\alpha+\beta+\gamma}{3} = 33.27 \end{cases}$

Ammonium Perchlorate

The crystals obtained of this salt were a little larger than those of the three preceding perchlorates, so that it was just possible to grind section plates and prisms for the optical work. The perfection was not so complete as with the smaller crystals of those other salts, but it was excellent in the cases of the crystals measured.

Crystal-System, Class and Space-Group.—The same as for potassium perchlorate and the other two salts of the group.

Forms observed.—$c\{001\}$, $m\{210\}$ or $\{110\}$ of old setting, $r\{101\}$ the $\{102\}$ of old setting all three well developed; $a\{100\}$, $b\{010\}$, $q\{011\}$, and $o\{211\}$ the $\{111\}$ of old setting, small, usually strips or spots.

Habit.—The most largely developed form was usually $m\{210\}$. Next came $c\{001\}$, and indeed this basal plane form sometimes predominated and conferred a tabular habit. The next was invariably $r\{101\}$, and usually as triangular little facets. The primary pinakoids $a\{100\}$ and $b\{010\}$ were never more than narrow strips. $q\{011\}$ and $o\{211\}$ were always small but several good, brilliantly reflecting little faces of these forms were present on some of the crystals measured. Fig. 8 represents a typical crystal.

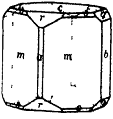


Fig. 8.—A Typical Crystal of Ammonium Perchlorate.

Axial Ratio.—$a : b : c = 1·5862 : 1 : 1·2807$, or $0·7931 : 1 : 1·2807$ for the old setting. Barker's values were $0·7932 : 1 : 1·2808$, an excellent agreement.

Crystal Angles.—Given in the accompanying table (p. 479).

Cleavage.—Perfect parallel $m\{210\}$ and very good parallel $c\{001\}$.

Density.—1·952 (Barker).

Molecular Volume.—$V = 60·19$ (Barker).

Topic Axial Ratios.—For true setting, by X-rays, $\chi = 4·9083$, $\psi = 3·0944$, $\omega = 3·9630$. For old setting (Groth-Barker), $\chi = 3·8957$, $\psi = 4·9120$, $\omega = 6·2909$.

Barker's values were 3·8959, 4·9117, 6·2909, the agreement being thus very satisfactory.

Optical Characters and Optic Axial Angle.—Groth (*loc. cit.*, p. 222) gives some approximate data; that the sign of the double refraction is positive, the plane

Angles of Ammonium Perchlorate

Angle	No. of measurements	Limits	Mean observed	Calculated	Difference	Barker's values
X ray Setting Old Setting		° ′ ° ′	° ′			′
am = (100) (210) or (100) (110)	4	38 17 - 38 30	38 23	38 25	2	—
mb = (210) (010) „ (110) (010)	4	51 34 - 51 35	51 35	51 35	0	—
mm = (210) (2$\bar{1}$0) „ (110) (1$\bar{1}$0)	10	76 46 - 76 54	76 50	—*	—	76 50
mm (210) ($\bar{2}$10) „ (110) ($\bar{1}$10)	14	103 4 - 103 18	103 11	103 10	1	—
ar = (100) (101) „ (100) (102)	11	50 57 - 51 9	51 5	51 5	0	—
rc = (101) (001) „ (102) (001)	27	38 48 - 39 3	38 55	*	—	38 55
rr = (101) (10$\bar{1}$) „ (102) (10$\bar{2}$)	7	102 6 - 102 16	102 11	102 10	1	—
bq = (010) (011) „ (010) (011)	2	38 0 - 38 0	38 0	37 59	1	—
qc = (011) (001) „ (011) (001)	6	51 50 - 52 9	52 0	52 1	1	52 1
ao = (100) : (211) (100) (111)		—		45 11	—	—
oq = (211) (011) „ (111) (011)				44 49	—	—
bo = (010) (211) „ (010) (111)		—		56 1		—
oo = (211) (2$\bar{1}$1) „ (111) (1$\bar{1}$1)				67 58	—	—
co = (001) (211) „ (001) (111)	11	64 4 - 64 11	64 9	64 7	2	—
om = (211) (210) „ (111) (110)	10	25 49 - 25 57	25 52	25 53	1	—
mr = (210) (101) „ (110) (102)	38	60 24 - 60 40	60 31	60 31	0	60 31
rm (101) ($\bar{2}$10) (102) ($\bar{1}$10)	37	119 24 - 119 36	119 29	119 29	0	—
mo = (210) (2$\bar{1}$1) „ (110) (1$\bar{1}$1)			—	78 10	—	—
om (2$\bar{1}$1) ($\bar{2}$10) (1$\bar{1}$1) ($\bar{1}$10)			—	101 50	—	—

of the optic axes is *c* {001}, and the acute bisectrix is the axis *b* This statement is the same as was made for potassium perchlorate, and is correct for ammonium perchlorate whereas it was incorrect for the potassium salt

Also that 2E is 111° 41′ for red light and 113° 23′ for blue that 2V = 68°, and the intermediate refractive index $\beta = 1\ 486$ These statements are correct as far as the approximate value of β is concerned, but the apparent optic axial angle in air is much larger than that stated

Three pairs of section plates were ground, perpendicular to the acute and obtuse bisectrices, and the final mean values of 2E, the optic axial angle in air, and $2V_a$, *the true angle within the crystal, afforded with them are given below*, for the determination of $2V_a$ by measurement of $2H_a$ and $2H_o$ the apparent acute and obtuse angles in a highly refractive liquid, α-monobromonaphthalene was used as the immersion liquid, as usual in the author's work

Optic Axial Angle of Ammonium Perchlorate

Light	2E	2V$_a$
	° ′	° ′
Li	124 8	69 31
C	124 18	69 34
Na	126 17	69 54
Tl	127 50	70 17
Cd	128 48	70 27
F	130 0	70 45

The true angle was confirmed by determinations during immersion in first turpentine and then toluene, the refraction of which is slightly lower and slightly higher than that of the crystals. The mean of the two determinations was 69° 16′ for sodium light.

Refractive Indices. Six prisms were used, four being 60°-prisms each ground to give two indices directly, with refracting edge parallel to one crystal-axis and the bisecting plane parallel to this and another crystal axis; the other two were formed by excellent little natural *m* faces, and yielded each both β and γ. The mean results are embodied in the table.

Refractive Indices of Ammonium Perchlorate

Light	α 2 M L Vibrations parallel axis *a*	β Vibrations parallel axis *c*	γ 1 M L Vibrations parallel axis *b*
Li	1·4794	1·4809	1·4855
C	1·4798	1·4813	1·4859
Na	1·4818	1·4833	1·4881
Tl	1·4840	1·4855	1·4904
Cd	1·4852	1·4868	1·4917
F	1·4865	1·4881	1·4931
G	1·4903	1·4919	1·4969

Mean Refractive Index for sodium light, $\frac{\alpha+\beta+\gamma}{3} = 1·4844$

Double Refraction, $Na_{\gamma-\alpha} = 0·0063$

General Formula for β, *in vacuo* —

$$\beta = 1·4733 + \frac{364\ 781}{\lambda^2} - \frac{128\ 900\ 000\ 000}{\lambda^4} + .$$

The formula also serves for α and γ, provided the constant is diminished and increased respectively by 0·0015 and 0·0048.

Molecular Optical Constants

		Specific			Molecular		
		α	β	γ	α	β	γ
Lorenz Refraction Constants	For C Light	0 1455	0 1459	0 1471	17 09	17 14	17 28
	,, G Light	0 1482	0 1486	0 1499	17 41	17 46	17 61
,, Dispersion		0 0027	0 0027	0 0028	0 32	0 32	0 33

Gladstone Molecular Refraction for C Light $\begin{cases} \alpha = 28\ 88,\ \beta = 28\ 97,\ \gamma = 29\ 25, \\ \text{Mean, } \dfrac{\alpha + \beta + \gamma}{3} = 29\ 03 \end{cases}$

Comparison of the Results for the Four Salts

These four perchlorates, of potassium, rubidium, cæsium, and ammonium all crystallise in the holohedral, rhombic bipyramidal, class (No 8 of the 32 classes of crystals) of the orthorhombic system, and in accordance with the detail arrangements of the Space Group V_h^{16} of Schoenflies They exhibit the same forms, and the faces, other than those rectangularly arranged, are inclined at angles so nearly alike that all four substances are represented by the same stereographic projection, shown in fig 9

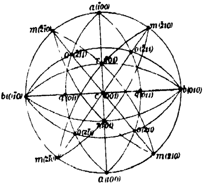


Fig 9 —Stereographic Projection of the Alkali Perchlorates

The Crystal-Axial Ratios These are compared below for the two settings

	For true setting as determined by X ray analysis			For old setting (Groth and Barker)			$\frac{a}{c}$ For old setting (for new setting double these values)
	a	b	c	a	: b	c	
$KClO_4$	0 7813	1	1 2807	1 5626	1 :	1 2807	0 6101
$RbClO_4$	0 7964	1	1 2884	1 5928	1	1 2884	0 6181
$CsClO_4$	0 8170 :	1	1 2970	1 6340	1 :	1 2970	0 6299
NH_4ClO_4	0 7931	1	1 2807	1 5862	1 :	1 2807	0 6193

The axial ratios of the crystals of the rubidium salt, for both settings, are thus intermediate between those of the crystals of the potassium and cæsium salts as already pointed out by Barker for the old setting

The ratios of the ammonium salt are such as bring it into the series without doubt, being within the limiting values for the three metallic salts

The Crystal Angles These are compared in the accompanying table

Comparison of the Crystal Angles

Angle X ray Setting	Old Setting	$KClO_4$	$RbClO_4$	$CsClO_4$	NH_4ClO_4
		° ′	° ′	° ′	° ′
am = (100) (210)	or (100) (110)	38 0	38 32	39 15	38 25
mb = (210) (010)	, (110) (010)	52 0	51 28	50 45	51 35
mm = (210) $(2\bar{1}0)$	, (110) $(1\bar{1}0)$	76 0	77 4	78 30	76 50
ar = (100) (101)	, (100) (102)	50 39	51 3	51 34	51 5
rc = (101) (001)	(102) (001)	39 21	38 57	38 26	38 55
rr = (101) $(10\bar{1})$	, (102) $(10\bar{2})$	101 18	102 6	103 8	102 10
bq = (010) (011)	, (010) (011)	37 50	37 49	37 38	37 59
qc = (011) (001)	, (011) (001)	52 1	52 11	52 22	52 1
ao = (100) (211)	, (100) (111)	44 45	45 14	45 54	45 11
oq = (211) (011)	,, (111) (011)	45 15	44 46	44 6	44 49
bo = (010) (211)	, (010) (111)	56 20	55 53	55 21	56 1
oo = (211) $(2\bar{1}1)$	,, (111) $(1\bar{1}1)$	67 20	68 14	69 18	67 58
co = (001) (211)	, (001) (111)	64 20	64 11	64 0	64 7
om = (211) (210)	, (111) (110)	25 40	25 49	26 0	25 53
mr = (210) (101)	(110) (102)	60 1	60 33	61 13	60 31
rm = (101) $(\bar{2}10)$	, (102) $(\bar{1}10)$	119 59	119 27	118 47	119 29
mo = (210) $(2\bar{1}1)$	,, (110) $(1\bar{1}1)$	77 24	78 23	79 41	78 10
om = $(2\bar{1}1)$ $(\bar{2}10)$	$(1\bar{1}1)$ $(\bar{1}10)$	102 36	101 37	100 19	101 50

The whole of the crystal angles of rubidium perchlorate lie between those of potassium and cæsium perchlorates The angles of ammonium perchlorate crystals are very close to those of rubidium perchlorate These two facts were stated by Barker, and are now fully confirmed by more extended measurements The three metallic salts thus form an excellent example of a eutropically isomorphous series, like the alkali sulphates and selenates

The next table summarises the angular differences in an interesting and very concise manner, by showing the average and maximum changes for each replacement To obtain the average change all the differences for the 18 angles recorded in the table, and for the same replacement, have been added together, irrespective of sign, and divided by 18 The maximum change is the largest of the angular changes brought about by the replacement in question.

Table of Average and Maximum Angular Changes

Replacement	Average Change	Maximum Change
K by Rb	32′	64 (1° 4′)
K by Cs	74′ (1° 14′)	150′ (2° 30′)
K by NH_4	27′	52′

The average change of angle on replacing potassium by cæsium is rather more than double that produced by replacing potassium by rubidium, and the introduction of ammonium instead of potassium causes a change which is only just slightly less than that brought about by the interchange of rubidium for potassium Exactly the same conclusions apply to the relations of the maximum changes, the absolute values of which are practically precisely double those of the average changes

Thus in every respect, as regards the changes in the crystal angles brought about by the interchange of one metallic family analogue for another, the changes are very nearly directly proportional to the change in the atomic weight or atomic number of the metal, that is, the angles of the three salts show a regular progression in the order of the atomic weight or atomic number of the alkali metal present *

Cleavage --Cleavages parallel to the basal plane c {001} and rhombic prism *m* {210} are common to all four salts of the series

Molecular Volume and Topic Axial Ratios --These are compared in the next table

Volume and Relative Cell Dimensions of Alkali Perchlorates

Salt	Molecular Volume	Topic Axial Ratios Old Setting (Barker)			Topic Axial Ratios New Setting by X ray Analysis		
		χ	ψ	ω	χ	ψ	ω
$KClO_4$	54 91	3 7408	4 7878	6 1318	4 7130	3 0161	3 8628
$RbClO_4$	61 33	3 9232	4 9262	6 3469	4 9429	3 1033 :	3 9982
$CsClO_4$	70 05	4 1621	5 0944 :	6 6074	5 2440	3 2093	4 1625
NH_4ClO_4	60 19	3 8957	4 9120	6 2909	4 9083	3 0944	3 9630

The values of the topic axial ratios for the old setting are very close to those obtained by Barker, given in the table on p 463 Again there is a regular progression in cell-volume and cell-edge dimensions when one alkali metal is replaced by another, both the molecular volume and the topic axial ratios (the latter also for both settings) of the rubidium salt being intermediate between the corresponding constants of the potassium and cæsium salts. Both molecular volume and topic axial ratios for the ammonium salt are close to the corresponding values for rubidium perchlorate indicating isostructure of the same close character as was observed with the sulphates, selenates and double sulphates and selenates of rubidium and ammonium.

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* The atomic numbers of K, Rb, and Cs are 19, 37, 55, the difference in each case being 18, corresponding to the number of electrons added to the atom, on passing from one element to the next of this family group of alkali metals

Conversion of the Relative Cell Dimensions into Absolute Dimensions.—The facts just mentioned were equally observed by Barker, to whom the molecular volumes are due, as the results derived from his topic axial ratios for the old setting, based on an assumed rhombic prismatic space-lattice. For they represented the dimensions of the unit cell of this lattice, in the axial directions, as already explained on p. 464.

Now it was shown on p. 463 that the structure and absolute cell dimensions of barytes have been unanimously agreed upon, by three parties of observers, in Germany, America, and this country, from detailed X-ray analysis, and the fact confirmed that potassium perchlorate is constructed on an analogous plan to barytes, as supposed by Barker, who regarded the whole group of alkali perchlorates and permanganates as isomorphous with the barytes group of minerals, as stated on p. 463.

As the topic axial ratios are strictly relative measures of the similar unit cells of the space-lattices of the whole isomorphous series, assuming the type of space lattice and nature of its unit cell to have been correctly diagnosed (as has been achieved in this case by X-ray analysis), given the absolute dimensions of the cells of any one member it should be possible by use of the topic axial ratios for the correct setting to calculate the absolute cell-dimensions of all the other members of the series. This will now be done for the perchlorates, knowing both the relative and the absolute dimensions of the rectangular orthorhombic space lattice cells of barytes.

Axial ratio of barytes—

given by Groth ('Chem. Kryst.,' II, 388), $a:b:c = 0{\cdot}8152:1:1{\cdot}3136$,

on same setting found by Wyckoff and Merwin by X-ray analysis, $a:b:c = 0{\cdot}8148:1:1{\cdot}3131$,

for true setting found by X-rays by W. and M., $a:b:c = 1{\cdot}633:1:1{\cdot}316$,

for true setting found by X-rays by James and Wood $a:b:c = 1{\cdot}6304:1:1{\cdot}3136$

Minimum Spacing of primary planes, Wyckoff and Merwin, for (100), 4·449 Å, for (010), 2·724 Å, for (001), 3·585 Å

Cell-edge dimensions for correct rectangular parallelepipedal cell (having double a)—

W. and M., $a = 8{\cdot}89$ Å, $b = 5{\cdot}45$ Å, $c = 7{\cdot}17$ Å
James and Wood, $a = 8{\cdot}85$ Å, $b = 5{\cdot}43$ Å, $c = 7{\cdot}13$ Å
*Mean of all observers, $a = 8{\cdot}87$ Å, $b = 5{\cdot}44$ Å, $c = 7{\cdot}15$ Å

Corresponding mean crystal axial ratios $a : b : c = 1{\cdot}632 : 1 : 1{\cdot}315$

*Topic axial ratios of barytes calculated for these mean axial ratios and using Barker's molecular volume 52·0, $\chi = 4{\cdot}7225$, $\psi = 2{\cdot}8937$, $\omega = 3{\cdot}8052$

*Corresponding topic axial ratios of potassium perchlorate $KClO_4$ (Tutton) $\chi = 4{\cdot}7130$, $\psi = 3{\cdot}0161$, $\omega = 3{\cdot}8628$

Cell edge dimensions of—

$KClO_4$ calculated from above starred data, $a = 8{\cdot}85$ Å, $b = 5{\cdot}67$ Å, $c = 7{\cdot}26$ Å
$RbClO_4$ similarly calculated from author's topic axial ratios, $a = 9{\cdot}28$ Å, $b = 5{\cdot}83$ Å, $c = 7{\cdot}51$ Å
$CsClO_4$ do do $a = 9{\cdot}84$ Å, $b = 6{\cdot}03$ Å, $c = 7{\cdot}81$ Å
NH_4ClO_4 do do $a = 9{\cdot}22$ Å, $b = 5{\cdot}82$ Å, $c = 7{\cdot}45$ Å

We have thus obtained the true absolute dimensions of the unit-cells of all the four alkali perchlorates. Moreover, it is possible to apply a critical test of their accuracy in one of the cases, potassium perchlorate, which will act as a test for the whole of them. For although owing to the smallness of the crystals James and Wood were unable to obtain intensity measurements of the X-ray reflections adequate to locate the positions of the atoms with certainty, they were able to measure the spacings without ambiguity, and to ascertain that the structure was truly analogous to that of barytes. The cell edge lengths thus found were, $a = 8{\cdot}81$ Å, $b = 5{\cdot}68$ Å, $c = 7{\cdot}22$ Å. These values only differ from the author's calculated ones by 0·01 for a and for b, and 0·04 for c, an agreement which is highly satisfactory, and shows that this new method of obtaining the absolute cell dimensions for all the other members of an isomorphous series, when the dimensions for one member of the series are known, is both trustworthy and highly accurate. Indeed it is comparable to the use of the anharmonic ratio of four poles in a zone, for calculating the position of any fourth face in a zone, given the position of the other three, and should prove equally useful, especially as only one member of the series is required to have been measured by X-rays.

The unit cells are thus seen progressively to increase in size in all three axial directions as potassium is replaced by rubidium and the latter in turn by cæsium. This is doubtless due, as pointed out for the sulphates of these alkali metals, to the increase in the size of the atoms of the alkali metal, eighteen electrons being added, either one or two whole shells of them (Langmuir or Bohr), when we pass from potassium to rubidium, and from the latter to cæsium. The cells of the ammonium salt are almost exactly of the same size as those of rubidium perchlorate.

Optical Characters and Optic Axial Angles.—The three metallic salts have the same optic axial plane, parallel $a\{100\}$, but the sign of the double refraction is positive for the potassium and rubidium salts and negative for cæsium perchlorate. The first median line (acute bisectrix) is the axis b in the potassium and rubidium salts, but the axis c in the cæsium salt. The measurements of optic axial angle afforded the following comparative results:—

True Optic Axial Angles of Alkali Perchlorates, $2V_a$.

Light	$KClO_4$	$RbClO_4$	$CsClO_4$	NH_4ClO_4
	° ′	° ′	° ′	° ′
Li	50 18	55 13	62 30 for all wave lengths	69 31
C	50 15	55 12		69 34
Na	49 48	55 4		69 54
Tl	49 28	54 55		70 17
Cd	49 9	54 44		70 27
F	48 48	54 33		70 45

The double refraction is feeble and the dispersion of the optic axes slight, so very small when the cæsium salt is reached that none at all could be measured, even with the thickest crystal plate obtained. Both the amount of dispersion of the optic axis and the size of the optic axial angle show a progression in the order of the atomic weights and atomic numbers of the three metals, the former diminishing and the latter increasing on passing from potassium perchlorate through the rubidium salt to the cæsium salt.

The ammonium salt differs in having $c\{001\}$ for the optic axial plane, its optic axes being separated at an angle $2V_a$ varying from 69° 31′ for Li light to 70° 45′ for greenish blue F hydrogen-light, the axis b being the acute bisectrix. The dispersion is intermediate between that for the potassium and rubidium salts, but opposite in direction.

Refractive Indices.—The refractive indices are compared in the next table. For all three metallic salts the α index corresponds to vibrations parallel to the crystal axis *c* the β index to vibrations along axis *a* and the γ index to vibrations along axis *b* The ammonium salt has the α and β vibrations reversed namely parallel respectively to the axes *a* and *c*

Refractive Indices of Alkali Perchlorates

Index	Light	$KClO_4$	$RbClO_4$	$CsClO_4$	NH_4ClO_4
α	Li	1 4708	1 4671	1 4730	1 4794
	C	1 4712	1 4674	1 4734	1 4798
	Na	1 4731	1 4692	1 4752	1 4818
	Tl	1 4749	1 4709	1 4771	1 4840
	Cd	1 4761	1 4720	1 4784	1 4852
	F	1 4774	1 4732	1 4797	1 4865
	G	1 4810	1 4767	1 4832	1 4903
β	Li	1 4714	1 4681	1 4766	1 4809
	C	1 4718	1 4684	1 4770	1 4813
	Na	1 4737	1 4701	1 4788	1 4833
	Tl	1 4755	1 4719	1 4808	1 4855
	Cd	1 4766	1 4730	1 4821	1 4868
	F	1 4779	1 4742	1 4835	1 4881
	G	1 4815	1 4777	1 4869	1 4919
γ	Li	1 4746	1 4712	1 4782	1 4855
	C	1 4750	1 4715	1 4786	1 4859
	Na	1 4769	1 4731	1 4804	1 4881
	Tl	1 4787	1 4750	1 4824	1 4904
	Cd	1 4799	1 4761	1 4837	1 4917
	F	1 4812	1 4774	1 4852	1 4931
	G	1 4848	1 4809	1 4887	1 4969
Mean Index $\frac{\alpha + \beta + \gamma}{3}$		1 4746	1 4708	1 4781	1 4844
Double Refraction Na $\gamma - \alpha$		0 0038	0 0039	0 0052	0 0063

The refractive indices of the three metallic salts are remarkably close to one another the differences only occurring in the third place of decimals and do not show the progression according to atomic number of alkali metal which is exhibited by the alkali sulphates where the differences are ten times as great In all the series of salts of these metals and double salts containing them investigated by the author the refractive indices of the potassium and rubidium salts have been very close sometimes overlapping It is only when the molecular refraction is considered that the real progression in refractive power becomes clearly revealed The indices of the ammonium salt are slightly higher than those of the cæsium salt

Molecular Optical Constants —The following tables show comparatively the results for the four salts

Molecular Refractions α, β, γ, and Dispersions, Lorenz, $\frac{n^2-1}{n^2+2}\ \frac{M}{d}$

Salt.	Light	α	Dispersion	β	Dispersion	γ	Dispersion
$KClO_4$	C G	15 35 15 63	0 28	15 37 15 64	0 27	15 46 15 73	0 27
$RbClO_4$	C G	17 03 17 32	0 29	17 06 17 35	0 29	17 16 17 45	0 29
$CsClO_4$	C G	19 61 19 95	0 34	19 73 20 08	0 35	19 79 20 15	0 36
NH_4ClO_4	C G	17 09 17 41	0 32	17 14 17 46	0 32	17 28 17 61	0 33

Molecular Refraction Gladstone, $\frac{n-1}{d}$ M, for C Light

Salt	α	β	γ	Mean, $\frac{\alpha+\beta+\gamma}{3}$
$KClO_4$	25 88	25 91	26 08	25 96
$RbClO_4$	28 67	28 73	28 92	28 77
$CsClO_4$	33 06	33 31	33 43	33 27
NH_4ClO_4	28 88	28 97	29 25	29 03

Specific Refractions and Dispersions Lorenz $\frac{n^2-1}{d\,(n^2+2)}$

Salt	Light	α	Dispersion	β	Dispersion	γ	Dispersion
$KClO_4$	C G	0 1108 0 1128	0 0020	0 1109 0 1129	0 0020	0 1115 0 1135	0 0020
$RbClO_4$	C G	0 0921 0 0937	0 0016	0 0923 0 0939	0 0016	0 0928 0 0944	0 0016
$CsClO_4$	C G	0 0844 0 0859	0 0015	0 0849 0 0864	0 0015	0 0852 0 0867	0 0015
NH_4ClO_4	C G	0 1455 0 1482	0 0027	0 1459 0 1486	0 0027	0 1471 0 1499	0 0028

From these tables it will be obvious that both the molecular refractions and dispersions, calculated either by the formula of Lorenz or that of Gladstone and Dale, and whether the individual α, β and γ values or their means are considered, exhibit a clear progression, following the order of the atomic numbers and atomic weights of the alkali metals The specific refractions and dispersions follow the same rule The molecular refraction of the ammonium salt is almost identical with that of the rubidium salt, a fact doubtless connected with their very close iso-structure The specific refraction and dispersion of the ammonium salt, like the refractive indices, are the highest in the series

Summary of Conclusions

An investigation of the crystals of the perchlorates of potassium, rubidium, cæsium and ammonium as regards their optical properties has been carried out for the first time, the difficulty of their very small size having been successfully overcome, and all the constants determined in detail for all parts of the spectrum The optical characters are similar, and both they and the optic axial angles, molecular and specific refractions and dispersions, of the three metallic salts, all show a regular progression, following the order of the atomic numbers (and atomic weights), similar to that observed with the alkali sulphates The refractive indices themselves are almost identical, being quite exceptionally close in this series (only differing in the third place of decimals), and do not show the progression It is brought out very clearly, however, in the molecular refractions

The ammonium salt differs as regards the position of the optic axial plane, which is $c\{001\}$ instead of $a\{100\}$, and its optic axial angle is larger than for the metallic salts The refractive index and the specific refraction are also larger The molecular refraction of ammonium perchlorate is nearly the same as that of rubidium perchlorate

A complete goniometrical measurement of the crystals has also been carried out, on a new "setting up," that indicated by the X-ray analysis of James and Wood, and the conclusions of Barker confirmed and amplified, while recorded both on the basis of his setting and on that of the true one determined by X-rays The whole of the crystal angles of rubidium perchlorate lie between those of potassium and cæsium perchlorates, these three salts forming a eutropic isomorphous series of the closest character, the angles following the order of progression of the atomic numbers of the alkali metals The maximum amount of angular change observed was 2° 30′, which occurred in the case of the rhombic prism angle between the potassium and cæsium salts The average change of angle between these two salts was slightly more than double the average change introduced by the replacement of potassium by rubidium The angles of ammonium perchlorate are very close to those of rubidium perchlorate, the average and maximum change on replacing potassium by the ammonium radicle being slightly less than when rubidium replaces potassium

The topic axial ratios have been calculated not only on the same assumption as Barker, of a rhombic prismatic space lattice, but on that indicated by X-ray analysis to be the correct one, the unit cell of which is a rectangular parallelepiped, the edges of which are parallel to the crystal axes and with the axis *a* of double the length of that for the old Groth Barker setting The same fact is clear, as given by Barker, that there is a regular progression, following the order of the metallic atomic numbers, in the topic axial ratios, and that these ratios for the ammonium salt are very close to those for the rubidium salt, indicating nearly complete iso-structure for the crystals of these two salts

Finally, a new principle has been used, to convert these relative cell-measures, the topic axial ratios, into absolute lengths, in Angstrom units, of the cell-edges It may be stated thus —

"In a well established isomorphous series, if any one member be thoroughly worked out by X-ray analysis, the crystals being large and perfect enough to permit not only of spacing determinations but of intensity measurements, so that the space-lattice unit-cell dimensions and character are fixed with certitude, then the absolute cell-dimensions of all the other members of the series may be obtained by calculation, from the topic axial ratios, which express the relative measures exactly, the crystal structure being strictly analogous throughout the series"

Now the barytes group of minerals and the perchlorates and permanganates of the alkalis have been shown to form a strictly structurally analogous isomorphous series and the structure of barytes, which forms excellent large transparent crystals eminently suitable for X-ray analysis and intensity measurements, has been thoroughly worked out and unanimously agreed upon by three independent parties of investigators, the structure being that of the Schoenflies space-group V_h^{16} of the holohedral orthorhombic crystal-class 8. Its cell-edge dimensions in Ångstrom units are thus known with certainty, and the mean values of the closely agreeing values given by Wyckoff and Merwin, and by James and Wood, have been used by the author to calculate the absolute cell dimensions of the alkali perchlorates, the crystals of which are very minute, unsuitable for thorough X-ray analysis These absolute cell-edge lengths show very clearly the progression with the atomic number of the alkali metal, and the iso-structure of the rubidium and ammonium salts

That the lengths of the cell-edges thus obtained are correct is capable of proof in one case, that of potassium perchlorate, of which James and Wood just succeeded in obtaining the spacing by X-ray analysis Their values agree most satisfactorily with the author's calculated ones The principle can therefore be accepted with confidence as remarkably trustworthy For it will often happen that one member of an isomorphous series may be eminently suitable for X-ray analysis, while the others, or some of them, are not

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The Theory of Ship Waves *

By E T Hanson, B A

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1 Summary

The theory of ship waves, when the sea is considered to be of infinite depth, has been the subject of many researches When the sea is of finite depth the integrals involved are more complicated but in this case also the theory has been worked out in considerable detail The main object of the present communication is to add to the number of cases which have been solved, or, to be more precise, which have been exactly formulated, a certain series in which the depth is variable

Of subsidiary interest, but coming under the title of the paper, are some considerations relating to the wave disturbance when the depth is finite These are dealt with briefly in section 5

Finally, in section 6, the problem of the wave disturbance at the surface of separation of two fluids of different density is briefly considered This problem is of much interest on account of observations made by Ekman Attention is here drawn to the similarity which exists between it and that of ship waves on a sea of finite depth

Reference should be made here to two very interesting papers by Lamb, in volume 31 of the 'Philosophical Magazine' (1916) p 386, on "Waves due to a Travelling Disturbance, with an application to Waves in Superposed Fluids," p 539, on "Wave Patterns due to a Travelling Disturbance"

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* The author is indebted to the Admiralty for permission to publish this paper

INTRODUCTION

The precise mode of disturbance of the water in the immediate neighbourhood of a ship is probably complicated It has not, hitherto, been possible to subject it to mathematical analysis, so that for the theoretical investigation of the disturbed motion of the water in the wake of the ship, some simpler cause of disturbance must be substituted for the ship itself

The simplest cause of disturbance, from the point of view of theory, is a pressure distribution acting on a small portion of the surface of the sea This pressure distribution is supposed to take the place of the ship, and to move with a velocity equal to that of the ship The actual functional representation of the distribution is, of necessity, somewhat ideal

Furthermore, after a sufficient lapse of time, all the phenomena which accompany the ship become steady In other words they are reproduced, without change, in each fresh part of the sea over which the ship advances Thus, if to both the sea and the ship is given a velocity equal and opposite to that of the ship, a state of steady motion throughout a uniformly flowing stream of great extent will be obtained

The most satisfactory method of treating problems dealing with surface waves on water would appear to consist in reducing the state to one of steady motion, whenever the nature of the problem allows of such treatment

2 PRELIMINARY THEORY

When an arbitrary distribution of pressure is applied to the surface of a stream, which, in the absence of the pressure, would flow with steady and uniform velocity, the flow becomes one of steady motion, but is indeterminate unless frictional forces between the particles of the fluid are introduced in order to damp out the free waves which may co-exist upon such a stream

The steady motion, which will finally be established, is that which is being sought, so that ultimately, when the general nature of the motion has been discovered, the effect of making these forces approach a vanishingly small value may be investigated It is thus not important that the law of the forces should be an absolutely natural one, and if it is one such as to simplify the analysis, those considerations are sufficient justification for adopting it Rayleigh assumed for the law of resistance that the departure of a particle from the state of steady motion was resisted by a force proportional to the relative velocity The simplification which this law introduces into the analysis arises from the fact that it does not destroy the irrotational nature of the motion.

The components of the force system acting upon a particle of the fluid, and the velocity components, are then derivable from potential functions It is proposed in this section to consider the preliminary theory for the case of finite depth The transition to the case of infinite depth, which is required in some of the problems, is readily made Let the undisturbed motion of the stream be one of uniform horizontal velocity c in a direction parallel to the positive direction of the axis of x, and let both the axes of x and y lie upon the undisturbed surface The axis of z is drawn vertically upwards The potential of the force system is denoted by Ω, the velocity potential by ϕ, and the frictional coefficient by τ It follows at once that Ω is expressed by the equation,

$$\Omega = gz - \tau(cx + \phi) \tag{1}$$

Let H be the depth of the stream, and let F be a function of x and y For the velocity potential the function assumed is

$$\frac{\phi}{c} = -x + \mathrm{B}\frac{\partial \mathrm{F}}{\partial x}\cosh \lambda(z + \mathrm{H}) \tag{2}$$

This expression makes $\partial\phi/\partial z$ vanish when $z = -\mathrm{H}$ If ζ be the surface elevation of the stream, the condition to be satisfied at the surface is

$$c\frac{\partial \zeta}{\partial x} = -\left[\frac{\partial \phi}{\partial z}\right]_{z=0}, \tag{3}$$

for $c\partial/\partial x$ may be written for $\partial/\partial t$ when the state has been reduced to one of steady motion

Let

$$\zeta = \mathrm{AF}$$

The condition (3) then becomes

$$c\mathrm{A}\frac{\partial \mathrm{F}}{\partial x} = -c\lambda\mathrm{B}\frac{\partial \mathrm{F}}{\partial x}\sinh \lambda\mathrm{H},$$

giving

$$\mathrm{A} = -\lambda\mathrm{B}\sinh \lambda\mathrm{H} \tag{4}$$

The equation for the pressure at any point may be written

$$p/\rho = \text{const} - gz + \tau(cx + \phi) - \tfrac{1}{2}q^2,$$

where ρ is the density of the fluid and q the resultant velocity at the point Since only small departures from the state of steady motion are under consideration, the squares of the velocities of the particles relatively to the undisturbed stream may be neglected Thus the pressure equation becomes

$$\frac{p}{\rho} = \text{const} - \tfrac{1}{2}c^2 - gz - \frac{c\mathrm{A}\cosh \lambda(z + \mathrm{H})}{\lambda \sinh \lambda\mathrm{H}}\left\{\tau\frac{\partial \mathrm{F}}{\partial x} + c\frac{\partial^2 \mathrm{F}}{\partial x^2}\right\}$$

Whence

$$-\frac{\Delta p}{\rho} = g\zeta + \frac{\tau c}{\lambda}\coth\lambda H\frac{\partial\zeta}{\partial x} + \frac{c^2}{\lambda}\coth\lambda H\frac{\partial^2\zeta}{\partial x^2}, \tag{5}$$

at the surface, where Δp represents the variable part of the pressure at the surface

It is now assumed that $\partial F/\partial x$ can be expanded in an infinite series of terms, each term consisting of products of the form

$$A_{\kappa\mu}\cos(\kappa x + \alpha)\cos(\mu y + \beta)$$

It then follows from equation (2) that, in order to satisfy the equation of continuity,

$$\kappa^2 + \mu^2 = \lambda^2$$

The pressure distribution at the surface may be very generally expressed by a corresponding series in the form of the double integral

$$\Delta p = \int_0^\infty\int_0^\infty f(\kappa,\ \mu)\cos\kappa x\cos\mu y\,d\kappa\,d\mu, \tag{6}$$

The particular integral solution of (6) is obtained by assuming for ζ the function

$$\tfrac{1}{2}\int_0^\infty\int_0^\infty f(\kappa,\ \mu)\{Ae^{i\kappa x} + Be^{-i\kappa x}\}\cos\mu y\,d\kappa\,d\mu,$$

where A and B are constants to be determined

It follows without difficulty that, corresponding to the pressure distribution on the surface given by (5), there is produced the surface form given by

$$\rho\zeta = \int_0^\infty\int_0^\infty f(\kappa,\ \mu)\left[\frac{(c^2\kappa^2/\lambda' - g)\cos\kappa x - (\kappa\tau c/\lambda')\sin\kappa x}{(c^2\kappa^2/\lambda' - g)^2 + (\kappa\tau c/\lambda')^2}\right]\cos\mu y\,d\kappa\,d\mu, \tag{7}$$

where $\lambda' = \lambda\tanh\lambda H$

The pressure distribution, which it is proposed to consider, is symmetrical about the origin, and is derived from the function

$$\Delta p = P/\sqrt{h^2 + r^2}, \tag{8}$$

in which $r^2 = x^2 + y^2$

A suitable expression for the pressure distribution, localised about a point, is given by

$$-\partial(\Delta p)/\partial h \tag{9}$$

The equation (8) is equivalent to

$$\Delta p = P\int_0^\infty e^{-h\lambda}J_0(r\lambda)\,d\lambda,$$

where J_0 is Bessel's function of zero order

But

$$J_0(r\lambda) = \frac{2}{\pi}\int_0^{\lambda} \frac{d\kappa \cos \kappa x \cos (y\sqrt{\lambda^2 - \kappa^2})}{\sqrt{\lambda^2 - \kappa^2}}$$

Hence

$$\Delta p = \frac{2P}{\pi}\int_0^{\infty}\int_0^{\infty} \frac{e^{-h\lambda}}{\lambda} \cos \kappa x \cos \mu y \, d\kappa \, d\mu, \tag{10}$$

so that $f(\kappa, \mu)$ of (6) is equal to $2Pe^{-h\lambda}/\pi\lambda$ in this case

Writing now—

$$\kappa = \lambda \cos \phi, \qquad \mu = \lambda \sin \phi, \qquad x = r \cos \theta, \qquad y = r \sin \theta,$$

equation (10) becomes

$$\Delta p = P/\pi \int_0^{\infty}\int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} d\lambda \, d\phi \cos \{\lambda r \cos (\phi - \theta)\} \, e^{-h\lambda} \tag{11}$$

This is most easily seen by considering that κ and μ are rectangular co-ordinates in a plane and λ, ϕ their corresponding polar co-ordinates

For convenience later write,

$$r \cos (\phi - \theta) = R$$

Considering an element of the integral (11) with respect to ϕ, there is obtained

$$\begin{aligned} \delta(\Delta p) &= \delta\phi P/\pi \int_0^{\infty} d\lambda \cos (\lambda R) \, e^{-h\lambda} \\ &= \delta\phi P/\pi \, \frac{h}{h^2 + R^2}, \end{aligned} \tag{12}$$

and it is readily verified that the integral of (12) with respect to ϕ is equal to the right hand side of (8)

The function $Ph/(h^2 + R^2)$ is a valid representation of a pressure localised along a line

Construct a figure and draw a line passing through the origin and making an angle ϕ with OX

Let ON be perpendicular to this line Let Q be the point r, θ Then, if N be the foot of the perpendicular from Q on ON,

$$QN = r \cos (\phi - \theta) = R \tag{13}$$

It will be assumed hereafter that H is unity The problem of ship waves on a sea of infinite depth has been more or less completely investigated, and it is therefore mainly intended to discuss here in detail the cases of finite and of variable depth The whole problem, including that of infinite depth, in all its features is, of course, reproduced by varying c

Let

$$g/c^2 \cos^2\phi = \mathrm{L} \quad \text{and} \quad \tau/\cos\phi = \mathrm{N} \tag{14}$$

Corresponding, then, to the pressure distribution given by (8), the equation (7) for the surface form can be expressed by

$$\rho\zeta = \frac{\mathrm{P}}{\pi g}\int_0^\infty\int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} e^{-h\lambda}\,d\lambda\,d\phi\,\mathrm{L}\left[\frac{(\lambda\coth\lambda-\mathrm{L})\cos\mathrm{R}\lambda-\mathrm{N}\coth\lambda\sin\mathrm{R}\lambda}{(\lambda\coth\lambda-\mathrm{L})^2+\mathrm{N}^2\coth^2\lambda}\right] \tag{15}$$

Considering, as before, a line element, it follows that

$$\frac{\rho\pi g}{\mathrm{P}}\frac{\partial\zeta}{\partial\phi} = \text{the real part of} \int_0^\infty \frac{\mathrm{L}\,d\lambda\,e^{i\mathrm{R}\lambda-h\lambda}}{\lambda\coth\lambda-\mathrm{L}-i\mathrm{N}\coth\lambda} \tag{16}$$

On introducing the complex variable $w = u + iv$ and writing

$$\mathrm{W} = \mathrm{U} + i\mathrm{V},$$

where

$$\mathrm{W} = \int_0^\infty \frac{\mathrm{L}\,dw\,e^{i\mathrm{R}w-hw}}{w\coth w-\mathrm{L}-i\mathrm{N}\coth w}, \tag{17}$$

then the function (16) under consideration is the value of U when the path of integration in (17) is the positive half of the real axis of w,

U having been written for $\dfrac{\rho\pi g}{\mathrm{P}}\dfrac{\partial\zeta}{\partial\phi}$

The singularities of the integrand in (17) are given by

$$w = \mathrm{L}\tanh w + i\mathrm{N}, \tag{18}$$

whence

$$u = \frac{\mathrm{L}\sinh 2u}{\cosh 2u+\cos 2v}, \tag{19}$$

$$v = \frac{\mathrm{L}\sin 2v}{\cosh 2u+\cos 2v} + \mathrm{N} \tag{20}$$

From these equations it follows that

$$2(v-\mathrm{N})\sinh 2u = 2u\sin 2v \tag{21}$$

Now, in accordance with the remarks made at the beginning, N is considered to be very small Under these circumstances

$$\frac{\sin 2v}{2(v-\mathrm{N})} < 1,$$

unless v is small, and therefore equation (21) cannot be satisfied for any real finite value of u unless v is small *Hence u must be zero except when v is small* But, if v be small, (19) may be written

$$u = \mathrm{L} \tanh u, \tag{22}$$

and this equation will be satisfied by $u = 0$ only if $\mathrm{L} < 1$ Hence in determining the roots, when $\mathrm{L} < 1$, u must be zero, and equation (20) becomes

$$\mathrm{V} = \mathrm{L} \tan v + \mathrm{N} \tag{23}$$

When $\mathrm{L} > 1$, v being small, (20) may be written in the form

$$v = \mathrm{L}v/\cosh^2 u + \mathrm{N},$$

so that

$$v = \mathrm{N}/(1 - \mathrm{L} \operatorname{sech}^2 u) \tag{24}$$

But, from (22), considering the function

$$f = u - \mathrm{L} \tanh u,$$

it follows that

$$\partial f/\partial u = 1 - \mathrm{L} \operatorname{sech}^2 u$$

It is obvious that, at the zero of this function, $\partial f/\partial u$ is positive Hence v, as given by (24), is positive It has been proved, then, that when a complex root exists, v being small, v is positive The indeterminateness in the problem is now removed and N may be diminished to zero The real root, which exists when $\mathrm{L} > 1$, must then be taken to lie in that quadrant in the plane of the complex variable w for which u and v are both positive

It is evident that, when N is zero, and $\mathrm{L} > 1$, the lowest imaginary root disappears When L is unity exactly, it is necessary to retain N in the whole investigation, a circumstance which will be referred to again

When N is zero, (17) becomes

$$\mathrm{W} = \int_0^\infty \frac{\mathrm{L}\, dw\, e^{i(\mathrm{R}-h)w}}{w \coth w - \mathrm{L}} \tag{25}$$

If, for the moment, the integrand be written in the form

$$\mathrm{I} = \mathrm{F}(w)/f(w),$$

and, if w_n be a root of $f(w)$, the theory of functions shows that the value of $\int \mathrm{I}\, dw$, when the path of integration is a small circle, whose centre is w_n, in the counter-clockwise direction, is

$$2\pi i \mathrm{F}(w_n)/f'(w_n) \tag{26}$$

In the present case

$$f'(w_n) = \frac{1}{w_n}\{\mathrm{L}(1 - \mathrm{L}) + w_n^2\} \tag{27}$$

$L < 1$ Consider first the case when $L < 1$ The roots of $f(w)$ are then all purely imaginary If R be positive in (25) the path of integration is taken along the imaginary axis from $i\infty$ to 0 and along the real axis from 0 to ∞ and round an arc of a quadrant of a circle of infinite radius If the path along the imaginary axis just excludes the singular points from the quadrant,

$$\int_{i\infty}^{0} \mathrm{I}\,dw + \int_{0}^{\infty} \mathrm{I}\,dw = 0 \tag{28}$$

But, if the closed path containing the singular points be considered,

$$\int_{0}^{i\infty} \mathrm{I}\,dw = \pi i\, \Sigma\, \mathrm{F}\,(iv_n)/f'\,(iv_n)\,, \tag{29}$$

whence

$$\int_{0}^{\infty} \mathrm{I}\,dw = \pi i\, \Sigma\, \mathrm{F}\,(iv_n)/f'\,(iv_n) \tag{30}$$

If R be negative, the path of integration must be taken to be round the quadrant for which u is positive and v negative It is easy to show, however, that equation (30) holds in this case also if only $-iv_n$ be written for iv_n in $\mathrm{F}\,(iv_n)$ On this understanding, only the positive imaginary roots need be considered

$L > 1$ Consider now the case when $L > 1$ If R be positive the path of integration must be round the quadrant in which u and v are both positive This quadrant, in accordance with the previous theory, is considered to contain the real singular point, and there is obtained, instead of (30),

$$\int_{0}^{\infty} \mathrm{I}\,dw = 2\pi i \mathrm{F}\,(u)/f'\,(u) + \pi i \sum_{1}^{\infty} \mathrm{F}\,(iv_n)/f'\,(iv_n), \tag{31}$$

where u is the real root, and $\sum\limits_{1}^{\infty}$ denotes summation of the imaginary roots except the first which is non-existent If R be negative, the integral becomes

$$\int_{0}^{\infty} \mathrm{I}\,dw = \pi i \sum_{1}^{\infty} \mathrm{F}\,(iv_n)/f'\,(iv_n) \tag{32}$$

The discussion of these integrals is reserved for the fifth section It may be noted, however, that, when c is small, the solution corresponds to that of great depth In this case the denominator of the integrand in (25) may be written

$$w - \mathrm{L}$$

3 THE THEORY OF WAVES ON A SEA BOUNDED BY A SLOPING SHORE

Very few cases of wave motion, when the depth is variable, appear to have been solved The theory of the two-dimensional oscillations of water, contained in a canal with sloping sides, was given by Kirchhoff in two particular cases In one case the sides of the canal are inclined at angles of 45° to the horizontal, and in the other case they are inclined at 30°

Two particular cases of the three-dimensional problem have been treated by Kelland and Macdonald* respectively The former found a solution for the propagation of waves along a canal whose sides are inclined at angles of 45° to the horizontal The latter has dealt with the problem of a canal whose sides are inclined at 30°

When the width of the canal is great the theory is simplified by considering the phenomena to take place on a sea bounded by a sloping shore It will be shown here that a much more general solution can always be obtained when the inclination of the shore to the horizontal is a submultiple of $\pi/2$ Thus when the inclination is 45°, 30°, 22½°, 18°, etc , the problem can be completely solved The solution includes the two-dimensional and the three-dimensional problems, referred to above when the canal is wide, as particular cases

The origin of co-ordinates is taken on the line in which the undisturbed water surface intersects the sloping shore This line is the axis of x The axis of z is drawn vertically upwards, and the axis of y is horizontal with its positive half lying upon the undisturbed water surface, forming a system of rectangular axes

The analytical problem involved is simple (*see* Lamb's 'Hydrodynamics,' page 438), and it can be shown that the velocity potential for a system of progressive waves may be expressed by the formula

$$\phi = \mathrm{P} \cos (\kappa x \pm \sigma t),$$

in which, if λ be the wave length, $\kappa = 2\pi/\lambda$, and if τ be the period, $\sigma = 2\pi/\tau$ Further P is independent of x and t Thus a condition of steady motion is possible by giving the water a steady uniform velocity in a direction parallel to its edge It is found that, for this particular type of waves, the requisite velocity is that of waves, of the prescribed wave length, on deep water

But another system of waves may become apparent when the shore is sloping The amplitude of these waves dies out exponentially from the edge, and becomes inappreciable at a distance whose projection on the slope exceeds a wave length A general formula for these edge waves was given by Stokes They are not concerned in the following problems Their velocity is given by the formula

$$c^2 = \frac{g}{\kappa} \sin \beta,$$

where β is the slope of the shore to the horizontal

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[*] "Waves in Canals," 'Proc Lond Math Soc,' vol XXV, p. 101 (1894)

The difficulty of the problems lies in the determination of the function P, which can, however, be effected in the cases to be now considered

The inclination of the shore to the horizontal is denoted by $-\theta_0$

It is assumed that the velocity potential when the motion is simple harmonic is given by

$$f(y, z) \cos \kappa x \cos (\sigma t + \epsilon)$$

or

$$f(y, z) \sin \kappa x \cos (\sigma t + \eta)$$

Progressive waves are thus possible and the theory can be developed by employing the artifice of steady motion Considering the first form, the factors $\cos \kappa x \cos (\sigma t + \epsilon)$ are, for brevity, omitted, and the function $f(y, z)$ is investigated

Consider the complex expression

$$\phi + i\psi = Ae^{(\lambda + i\mu)y + (\alpha + i\beta)z + i\epsilon} \tag{33}$$

The real or the imaginary part of this expression represents the function $f(y, z)$ The equation of continuity is satisfied if

$$(\lambda + i\mu)^2 + (\alpha + i\beta)^2 = \kappa^2 \tag{34}$$

This condition is satisfied if

$$\begin{aligned} \lambda &= \kappa p \cos \theta_1 & \quad\text{or}\quad && \lambda &= \kappa p \cos \theta_1 \\ \alpha &= \kappa p \sin \theta_1 & && \alpha &= -\kappa p \sin \theta_1 \\ \mu &= -\kappa q \sin \theta_1 & && \mu &= -\kappa q \sin \theta_1 \\ \beta &= \kappa q \cos \theta_1 & && \beta &= -\kappa q \cos \theta_1 \end{aligned}$$

For then $\lambda\mu + \alpha\beta = 0$

Further, on writing

$$p = \cosh \omega$$
$$q = \sinh \omega,$$

the real part of (34), viz

$$\lambda^2 + \alpha^2 - \mu^2 - \beta^2 = \kappa^2,$$

is satisfied

Now, if for y is written $r \cos \theta$ and for z $r \sin \theta$, the condition to be satisfied at the sloping bank is

$$\partial\phi/r\partial\theta = 0 \qquad \text{when } \theta = \theta_0,$$

where ϕ is the velocity potential of the motion

The surface condition is satisfied if

$$\sigma^2\phi = g\, \partial\phi/r\, \partial\theta,$$

when $\theta = 0$

Alternatively, if ψ be the velocity potential, similar conditions must be fulfilled The equation (33) may be written in the forms

$$\phi + \iota\psi = \mathrm{A} \exp\,[\kappa r \cosh\omega \cos(\theta_1 - \theta) - \iota\kappa r \sinh\omega \sin(\theta_1 - \theta) + \iota\epsilon], \quad (35\text{A})$$

or

$$\phi + \iota\psi = \mathrm{A} \exp\,[\kappa r \cosh\omega \cos(\theta_1 + \theta) - \iota\kappa r \sinh\omega \sin(\theta_1 + \theta) + \iota\epsilon] \quad (35\text{B})$$

On differentiating these equations it follows that

$$\partial(\phi + \iota\psi)/\kappa r \cosh\omega\,\partial\theta = +[\sin(\theta_1 - \theta) + \iota \tanh\omega \cos(\theta_1 - \theta)](\phi + \iota\psi), \quad (36\text{A})$$

or

$$\partial(\phi + \iota\psi)/\kappa r \cosh\omega\,\partial\theta = -[\sin(\theta_1 + \theta) + \iota \tanh\omega \cos(\theta_1 + \theta)](\phi + \iota\psi) \quad (36\text{B})$$

The surface condition requires that

$$\sigma^2(\phi + \iota\psi) = \kappa g \cosh\omega \quad \partial(\phi + \iota\psi)/\kappa r \cosh\omega\,\partial\theta$$

Hence, if $\sigma^2 = \kappa g \cosh\omega$, the surface condition will be satisfied if

$$\phi + \iota\psi = \partial(\phi + \iota\psi)/\kappa r \cosh\omega\,\partial\theta, \text{ when } \theta = 0 \quad (37)$$

If $\theta_1 = \frac{1}{2}\pi$ in (35A) and its derivative (36A), it is obvious that (37) is satisfied

Consider, therefore, the series obtained as follows, in which (35A) with $\theta_1 = \frac{1}{2}\pi$ constitutes the first term

$$\left.\begin{aligned}
(\phi + \iota\psi)_1 &= \mathrm{A}_1 \exp\,[\kappa r \cosh\omega \sin\theta - \iota\kappa r \sinh\omega \cos\theta], \\
(\phi + \iota\psi)_2 &= \mathrm{A}_2 \exp\,[\kappa r \cosh\omega \sin(2\theta_0 - \theta) \\
&\qquad - \iota\kappa r \sinh\omega \cos(2\theta_0 - \theta)], \\
(\phi + \iota\psi)_3 &= \mathrm{A}_3 \exp\,[\kappa r \cosh\omega \sin(2\theta_0 + \theta) \\
&\qquad - \iota\kappa r \sinh\omega \cos(2\theta_0 + \theta)], \\
\\
(\phi + \iota\psi)_{2n} &= \mathrm{A}_{2n} \exp\,[\kappa r \cosh\omega \sin(2n\theta_0 - \theta) \\
&\qquad - \iota\kappa r \sinh\omega \cos(2n\theta_0 - \theta)] \\
(\phi + \iota\psi)_{2n+1} &= \mathrm{A}_{2n+1} \exp\,[\kappa r \cosh\omega \sin(2n\theta_0 + \theta) \\
&\qquad - \iota\kappa r \sinh\omega \cos(2n\theta_0 + \theta)]
\end{aligned}\right\} \quad (38)$$

The solution consists of the sum of these terms, and the A's are, in general, complex coefficients

For an even term

$$\frac{\partial(\phi + \iota\psi)_{2s}}{\kappa r \cosh\omega\,\partial\theta} = -\mathrm{A}_{2s}[\cos(2s\theta_0 - \theta) + \iota \tanh\omega \sin(2s\theta_0 - \theta)]\frac{(\phi + \iota\psi)_{2s}}{\mathrm{A}_{2s}}, \quad (39\text{A})$$

and for an odd term

$$\frac{\partial (\phi + i\psi)_{2s+1}}{\kappa r \cosh \omega \, \partial \theta} = A_{2s+1} [\cos (2s\theta_0 + \theta) + i \tanh \omega \sin (2s\theta_0 + \theta)] \frac{(\phi + i\psi)_{2s+1}}{A_{2s+1}} \tag{39B}$$

When $s = 0$ (39B) represents the first term, and this term, as already specified, satisfies the surface condition If $(2n + 1)\,\theta_0 = -\frac{1}{2}\pi$, and if the coefficient A_{2n+1} be purely real, the last term will satisfy the condition at the sloping boundary if ϕ be the velocity potential

The first and second terms together satisfy the boundary condition if $A_1 = A_2$ The third and fourth if $A_3 = A_4$, and so on

The surface condition is fully satisfied if

$$A_{2s} + A_{2s+1} = (-A_{2s} + A_{2s+1}) (\cos 2s\theta_0 + i \tanh \omega \sin 2s\theta_0),$$

so that there are $2n$ equations to determine the $2n$ necessary coefficients

If $2n\theta_0 = -\frac{1}{2}\pi$, the last term is omitted It is only necessary, therefore, to find the condition that the penultimate term should satisfy the surface condition Let

$$A_{2n} = B_{2n} + iC_{2n}$$

When $\theta = 0$,

$$(\phi + i\psi)_{2n} = (B_{2n} + iC_{2n})\, e^{-\kappa r \cosh \omega},$$

and

$$\frac{\partial (\phi + i\psi)_{2n}}{\kappa r \cosh \omega \, \partial \theta} = (B_{2n} + iC_{2n})\, i \tanh \omega \, e^{-\kappa r \cosh \omega}$$

Hence, if ϕ be the velocity potential, it is necessary to write

$$B_{2n} = -C_{2n} \tanh \omega$$

Some special cases of these equations will be given now for future reference

Two-Dimensional Waves If ω be increased indefinitely while κ is correspondingly diminished, so that ultimately

$$\kappa \cosh \omega = \kappa \sinh \omega = \mu, \text{ say},$$

and

$$\tanh \omega = 1,$$

the solution is obtained of two-dimensional standing waves upon a sloping bank

If $2\theta_0 = -\frac{1}{2}\pi$

$$(\phi + i\psi)_1 = A\,(1 - i)\,\{e^{\mu r \sin \theta - i\mu r \cos \theta}\},$$

$$(\phi + i\psi)_2 = A\,(1 - i)\,\{e^{-\mu r \cos \theta + i\mu r \sin \theta}\}$$

The required solution is $\phi_1 + \phi_2$, obtained by taking the sum of the real parts of the right hand sides

If $3\theta_0 = -\frac{1}{2}\pi$, then, when $\theta = 0$

$$(\phi + i\psi)_1 = Aie^{-i\mu y},$$

$$(\phi + i\psi)_2 = Aie^{-\sqrt{3}/2\,\mu y + \frac{1}{2}i\mu y},$$

$$(\phi + i\psi)_3 = -A\sqrt{3}e^{-\sqrt{3}/2\,\mu y - \frac{1}{2}i\mu y}$$

Hence the expression for the surface elevation in this case become

$$A\left[\sin\mu y + 2e^{-\frac{\sqrt{3}}{2}\mu y}\sin\left(\tfrac{1}{2}\mu y - \frac{\pi}{3}\right)\right] \tag{40}$$

Three dimensional Cases when $\omega = 0$. When $\theta_0 = -30°$

$$\phi = A\left[e^{\kappa r\sin\theta} + e^{\kappa r\sin(2\theta_0-\theta)} - \frac{1+\cos 2\theta_0}{1-\cos 2\theta_0}e^{\kappa r\sin(4\theta_0+\theta)}\right]$$

When $\theta_0 = -18°$ the value of ϕ when $\theta = 0$ is given by

$$\phi = A\left[1 + e^{\kappa y\sin 2\theta_0} - \frac{1+\cos 2\theta_0}{1-\cos 2\theta_0}e^{\kappa y\sin 2\theta_0}\right.$$

$$\left. - \frac{1+\cos 2\theta_0}{1-\cos 2\theta_0}e^{\kappa y\sin 4\theta_0} + \frac{1+\cos 2\theta_0}{1-\cos 2\theta_0}\,\frac{1+\cos 4\theta_0}{1-\cos 4\theta_0}e^{\kappa y\sin 4\theta_0}\right] \tag{41}$$

If the expression on the right hand side of (41) vanishes for one or more values of y there will be longitudinal nodes parallel to the edge of the shore.

To find these longitudinal nodes the equation to be solved is

$$1 - \frac{2\cos 2\theta_0}{1-\cos 2\theta_0}p + \frac{1+\cos 2\theta_0}{1-\cos 2\theta_0}\,\frac{2\cos 4\theta_0}{1-\cos 4\theta_0}p^{2\cos 2\theta_0} = 0$$

where $p = e^{\kappa y\sin 2\theta_0}$.

In these problems it may be observed that if the motion be made steady by imparting a uniform velocity to the water parallel to its bank, then at some distance from the edge the steady motion is sensibly the same as that of a current flowing in a deep canal of rectangular section. With $\theta_0 = -18°$ equation (41) becomes

$$\phi = A\{1 - 8{\cdot}48p + 8{\cdot}53p^{1{\cdot}61}\},$$

with $p = e^{-\kappa y(0{\cdot}59)}$.

ϕ has a maximum (negative) value when $p = 0{\cdot}45$ and this makes

$$\phi_{\max} = -A(0{\cdot}86).$$

The zeros of ϕ/A are found to be given by $p = 0{\cdot}19$ and $p = 0{\cdot}76$.

A graph of the wave section by a plane at right angles to the edge of the bank, passing through a crest of the sensibly undisturbed waves at a distance from the edge, and showing the two nodes with the inversion between them, is represented in fig 1 by the broken curve The full curve represents a section through a trough of the distant waves

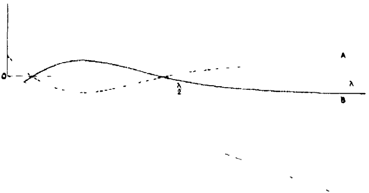

Fig 1

The distances of the nodes from the edge are 0 07 λ and 0 45 λ respectively

General Case when $\theta_0 = -30°$ —For this case the first three terms of (38) are required Let

$$A_1 = A_2 = Ae^{i\epsilon},$$

and let $A_3 = AB$, where A and B are real It is then found that

$$Be^{-i\epsilon} = \frac{C+1}{C-1}$$

where

$$C = \cos 2\theta_0 + i \tanh \omega \sin 2\theta_0$$

The function required is ϕ, and when $\theta = 0$, putting $r = y$,

$$\phi = A\left[\cos(\kappa y \sinh \omega - \epsilon) + e^{\kappa y \cosh \omega \sin 2\theta_0} \cos(\kappa y \sinh \omega \cos 2\theta_0 - \epsilon)\right.$$
$$\left. + Be^{\kappa y \cosh \omega \sin 2\theta_0} \cos(\kappa y \sinh \omega \cos 2\theta_0)\right] \qquad (42)$$

General case when $\theta_0 = -45°$ —For this case the first two terms of (38) are required Let

$$A_1 = A_2 = Ae^{i\epsilon}$$

It is found, then, that

$$\cot \epsilon = -\tanh \omega.$$

The function required is ϕ, and, when $\theta = 0$, putting $r = y$,

$$\phi = A\left[\cos \epsilon \; e^{-\kappa y \cosh \omega} + \cos(\kappa y \sinh \omega - \epsilon)\right] \qquad (43)$$

4 Ship Waves on a Sea Bounded by a Sloping Shore

The first problem to be considered is that of ship waves near the shore of a beach which slopes at an angle of 30° to the horizontal The undisturbed water has a uniform steady flow parallel to the edge of the shore and in the positive direction of the axis of x An approximately concentrated pressure distribution is applied at, and in the neighbourhood of, a point near the shore The resulting disturbed motion of the water surface is investigated

For this purpose it is necessary to employ equation (42) It is readily found, from the expressions for B and C, that

$$\mathrm{B}e^{-i\epsilon} = \frac{1 + i \tanh \omega\,(\cot \theta_0 + \tan \theta_0) - \tanh^2 \omega}{\tan^2 \theta_0 + \tanh^2 \omega} \tag{44}$$

From this it follows that

$$\tan \epsilon = \frac{2}{\sqrt{3}} \sinh 2\omega$$

since

$$\sin 2\theta_0 = -\sin \pi/3$$

By giving all possible values to ω it is seen that ϵ lies between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$. Since $\tanh \omega$ is always less than unity it follows from (44) that B must be negative

It is not difficult to show that, writing for the moment $p = \frac{1}{2}\kappa y \sinh \omega$,

$$\cos (p - \epsilon) + \mathrm{B} \cos p = \mathrm{D} \cos (p - \gamma),$$

in which

$$\mathrm{D} \cos \gamma = \cos \epsilon + \mathrm{B}$$

and

$$\mathrm{D} \sin \gamma = \sin \epsilon$$

It follows that $\mathrm{D}^2 = 4$, and that, since B is negative, D must be also negative Hence

$$\mathrm{D} = -2$$

Further ϵ and γ must be opposite in sign

The equation (42) now reduces to

$$\phi = \mathrm{A}\,[\cos (\kappa y \sinh \omega - \epsilon) - 2e^{-\sqrt{3}/2\ \kappa y \cosh \omega} \cos (\tfrac{1}{2}\kappa y \sinh \omega - \gamma)], \tag{45}$$

where

$$\left.\begin{aligned} \tan \epsilon &= 2/\sqrt{3}\ \sinh 2\omega \\ \sin \gamma &= -\tfrac{1}{2} \sin \epsilon \end{aligned}\right\}. \tag{46}$$

and

It is convenient to write

$$\kappa \sinh \omega = \mu, \qquad \kappa \cosh \omega = \lambda,$$

so that

$$\kappa^2 + \mu^2 = \lambda^2$$

For the moment write

$$M = 2e^{-\sqrt{3}/2\ \kappa y \cosh \omega},$$

then it can be shown without difficulty that ϕ is expressible in a form suitable for the problem under consideration Multiply ϕ by the factor $2 \cos \mu a$, then $2 \cos \mu a\ \ \phi/A$ can be expressed as the sum of the eight terms —

$$\left.\begin{array}{llll} 1 & \cos \mu\,(y-a) \cos \epsilon & 2 & \cos \mu\,(y+a) \cos \epsilon \\ 3 & \sin \mu\,(y-a) \sin \epsilon & 4 & \sin \mu\,(y+a) \sin \epsilon \\ 5 & -\mathrm{M} \cos \mu\,(\tfrac{1}{2}y-a) \cos \gamma & 6 & -\mathrm{M} \cos \mu\,(\tfrac{1}{2}y+a) \cos \gamma \\ 7 & -\mathrm{M} \sin \mu\,(\tfrac{1}{2}y-a) \sin y & 8 & -\mathrm{M} \sin \mu\,(\tfrac{1}{2}y+a) \sin \gamma \end{array}\right\} \qquad (47)$$

The factor $2 \cos \mu a$ is immaterial, and it may be said that the sum of these eight terms, multiplied by some constant A, represents the surface value of ϕ for a possible mode of motion when the shore is inclined at 30° to the horizontal There is a doubly infinite number of possible modes obtained by giving different values to ω and to λ

It is advantageous to write now,

$$\kappa = \lambda \cos \phi, \qquad \mu = \lambda \sin \phi,$$

whence

$$\cosh \omega = \sec \phi,$$

and

$$\sinh \omega = \tan \phi$$

Here ϕ is an angle and will cause no confusion with the potential function, which no longer appears explicitly in the present problem The possible modes of motion are determined by λ and ϕ

Multiply the first term of (47) by

$$\frac{2\mathrm{P}}{\pi} \cos \kappa x\ \ \frac{1}{\lambda} e^{-h\lambda}, \qquad (48)$$

and consider the double integral

$$\mathrm{I}_1 = \frac{\mathrm{P}}{\pi} \int_0^\infty \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} d\lambda\, d\phi \cos \{\lambda r \cos (\phi - \theta)\} \cos \epsilon\ \ e^{-h\lambda}, \qquad (49)$$

where (r, θ) are the polar co-ordinates of a point referred to $(0, a)$ as origin, θ being measured in the counterclockwise direction from the positive direction of the axis of x

If the third, fifth, and seventh terms of (47) be treated in the same way, it is not difficult to show that $-\partial \mathrm{I}_1/\partial h$ is the only term which gives a finite pressure anywhere namely at the point (0 a) when h is reduced without limit

If the even terms of (47) be multiplied by the factor (48) similar results obtain In fact the point (0 a) is the exact image for the whole surface motion of the point (0 a) in the line $y = 0$ It is only necessary to consider therefore the odd terms the even terms being a simple reflection

It has been proved then that the function $-\partial I/\partial h$ where

$$I = \frac{2P}{\pi}\left[\int_0^\infty d\kappa\cos\kappa x \;\; \cos\{\mu(y-a)-\epsilon\}\int_0^\infty \frac{1}{\lambda}e^{-\lambda h}d\mu \right.$$
$$\left. -\,2\int_0^\infty d\kappa\cos\kappa x \;\; M\cos\{\mu(y-2a)-\gamma\}\int_0^\infty \frac{1}{\lambda}e^{-\lambda h}d\mu\right] \qquad (50)$$

is very small when h is small at all points of the water surface except near the point (0 a) Some steps in the theory are here omitted but it may be stated that Lord Rayleigh's artifice of introducing a small frictional resistance between the particles of the fluid is employed in order to make the problem determinate The process by which the surface form is obtained when the surface pressure distribution is given is a simple modification of that outlined in the second section where the complete treatment of finite depth will be found The reason for putting the pressure distribution in the form (50) will then be apparent As in that section the coefficient of the frictional resistance which is proportional to the relative velocity of a particle with respect to the state of steady motion is denoted by τ The pressure distribution (50) will be denoted by $\Delta p_1 - \Delta p_2$ and the wave form due to Δp_1 will be considered first If ζ_1 be the surface elevation due to Δp_1 when the problem has been reduced to one of steady motion it follows that $\rho\zeta_1 \rightarrow$ the real part of

$$\frac{P}{\pi}\int_0^\infty\int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi}\frac{\lambda e^{-\lambda h}d\lambda d\phi}{c\cos\phi}\;\frac{e^{i\lambda r\cos(\phi-\theta)}}{\lambda-\beta} \qquad (51)$$

where ρ is the density of the fluid and

$$\beta = \frac{g}{c^2\cos^2\phi} + \frac{i\tau}{c\cos\phi}$$

Let R denote $r\cos(\phi-\theta)$ and for λ write the complex variable $w = u + iv$ so that $\lambda = u$

Let $\delta\zeta_1$ denote the infinitesimal part of ζ_1 due to an element $\delta\phi$ The expression (51) is a somewhat complicated function of ϕ but when ϕ is constant ϵ is constant Consider therefore the expression

$$\frac{P}{\rho\pi}\frac{e^{i\epsilon}}{c^2\cos^2\phi}\delta\phi\int_0^\infty\frac{we^{iRw-hw}}{w-\beta}dw \qquad (52)$$

The real part of (52), when the integral is taken along the positive half of the real axis of w, represents $\delta\zeta_1$ This is in reality the disturbance produced by a line of pressure athwart the stream The frictional coefficient τ serves its purpose by showing that β lies in the quadrant for which both u and v are positive, since $\cos\phi$ is positive between the limits of integration Consider in the first place that R is positive, or in other words that $\phi-\theta$ lies between 0 and $+(\pi/2)$ or 0 and $-(\pi/2)$ In this case both u and v must be positive, in order to ensure the validity of the ensuing contour integration

Denoting the integrand in (52) by wF, and observing that wF vanishes round that portion of an infinite circle which lies in the quadrant for which u and v are positive, it follows that

$$\int_{i\infty}^{0} w\mathrm{F}\,dw + \int_{0}^{\infty} w\mathrm{F}\,dw - 2\pi i\beta e^{(i\mathrm{R}-h)\beta} = 0 \tag{53}$$

In the second place let R be negative

In this case

$$\int_{\infty}^{0} w\mathrm{F}\,dw + \int_{0}^{-i\infty} w\mathrm{F}\,dw = 0,$$

corresponding to the event of $\phi-\theta$ lying between π and $+(\pi/2)$ or π and $-(\pi/2)$

A Pressure Line athwart the Stream—Before proceeding further with the theory of ship waves due to a pressure point, some progress can be made with the somewhat simpler theory of a pressure line

Reducing τ to zero and assuming, in the first place, that R is positive, the expression to be considered is

$$\begin{aligned} \mathrm{I}_1 + i\mathrm{J}_1 &= -\int_{i\infty}^{0} \mathrm{F}\,dw \\ &= \int_{0}^{\infty} \frac{e^{-v\mathrm{R}-ivh}}{v+i\beta}\,dv. \end{aligned} \tag{54}$$

When R is negative, the expression to be considered is

$$\begin{aligned} \mathrm{I}_2 + i\mathrm{J}_2 &= \int_{0}^{-i\infty} \mathrm{F}\,dw \\ &= \int_{0}^{\infty} \frac{e^{v\mathrm{R}+ivh}}{v-i\beta}\,dv \end{aligned} \tag{55}$$

The integral (54) is of some celebrity in the history of mathematics. Writing for the moment $\mathrm{R}+ih=a$,

$$\mathrm{I}_1 + i\mathrm{J}_1 = \int_{0}^{\infty} \frac{e^{-av}}{v+i\beta}\,dv,$$

which can be expanded in the form

$$I_1 + iJ_1 = e^{i\beta a}\left\{-\gamma - \log(i\beta a) + i\beta a + \frac{\beta^2 a^2}{2\,\underline{|2}} - \frac{i\beta^3 a^3}{3\,\underline{|3}} - \right\}, \qquad (56)$$

γ being Euler's constant 0 5772 This expansion is suitable when both R and h are small, in which case, considering only the real part, the following expression results —

Writing, for brevity, $x = R\beta$, $y = h\beta$,

$$I_1 = -Ce^{-y}\cos x + \left(\frac{\pi}{2} - S\right)e^{-y}\sin x, \qquad (57)$$

in which

$$C = \gamma + y + \tfrac{1}{2}\log(x^2 + y^2) - \tfrac{1}{4}x^2 + \tfrac{1}{4}y^2 \quad ,$$

and

$$S = x + \tfrac{1}{2}xy - \tan^{-1} y/x \quad ,$$

When $y = 0$, C = the known function Ci, and S = the known function Si

When R is large a suitable semi-convergent series can be obtained for the integral, but it is advantageous to proceed as follows

It can be shown that

$$I_1 = -M + N,$$

where

$$M = \int_0^\infty \frac{ve^{-vR}\cos vh}{v^2 + \beta^2}\,dv, \qquad (58)$$

and

$$\partial N/\partial(h\beta) = M \qquad (59)$$

The process which follows sets out to find, if possible, a simple expression for the value of the integral when R is neither very large nor very small When $h = 0$, the value can be calculated by means of the tabulated functions Ci and Si Hence, in this case, it is possible to test the nature of the approximation involved by substituting such a simple expression for the accurate one

Consider the function

$$f_1 = \frac{v}{v^2 + \beta^2},$$

and compare it with the function

$$f_2 = ve^{-v/\beta+1}/2\beta^2$$

Both of these functions are zero at the origin and tend to zero as $v \to \infty$ Both have a maximum when $v = \beta$, and the common value at this point is $1/2\beta$ The function f_2 increases, however, a little more rapidly than f_1 before the maximum is reached, and decreases more rapidly than f_1 after the maximum is passed

Let

$$M' = \int_0^\infty f_2 e^{-vR} \cos vh \, dv$$

If h is small compared with R, the effect of cos vh upon either integral M or M′ is very small For small values of R that part of the integral M, for which v is large, will predominate, consequently M′ will be somewhat smaller than the true value For large values of R that part of the integral M′, which lies between $v = 0$ and $v = \beta$, will predominate, consequently M′ will be somewhat larger than the true value

There is, therefore, a value of R for which M = M′

Now, when h is neglected, the function M can be expressed in terms of the irreducible transcendental functions Ci and Si which have been tabulated The value of the function M′ is

$$M' = \frac{e}{2} \frac{(1 + R\beta)^2 - h^2\beta^2}{\{(1 + R\beta)^2 + h^2\beta^2\}^2}, \tag{60}$$

which, when h is neglected, reduces to

$$M' = \frac{e}{2} \frac{1}{(1 + R\beta)^2}$$

Under these circumstances it is found that the value of Rβ, which makes M = M′, lies in the vicinity of unity A further comparison shows that, so long as $R\beta > \frac{1}{2}$, M may be replaced by M′ to a sufficiently high degree of approximation, since, for large values of Rβ, both integrals rapidly become evanescent

It will be noted that the neglect of h in (60) involves only the square of h, so that, retaining the first power of h, which is small compared with R, it may be concluded from (59) and (60) that, very approximately,

$$M = \frac{e}{2} \frac{1}{(1 + R\beta)^2}$$

and

$$N = \frac{e}{2} \frac{h\beta}{(1 + R\beta)^2},$$

when

$$R\beta > \tfrac{1}{2}$$

Whence

$$I_1 = -\frac{e}{2} \frac{1 - h\beta}{(1 + R\beta)^2} \tag{61}$$

when $R\beta > \frac{1}{2}$

An approximation for the real part of (52) may now be written down but the most interesting case is that in which ϕ and therefore ϵ is zero that is when the line of pressure is at right angles to the shore The consideration of the effect of Δp_2 follows the same lines and it can be shown that the resulting disturbance decreases rapidly as the distance from the edge of the shore increases

It will be noted that Δp is now not everywhere negligible when h is very small but becomes comparable with Δp_1 when both x and y are very small Suppose that a small obstruction is placed around the origin then the line of pressure on the fluid may be considered sensibly uniform Thus the disturbances at some distance from the origin due to both Δp_1 and Δp exist and in addition, a local disturbance due to the obstruction At a moderate distance from the origin the latter disturbance is negligible Hence the motion at points not too close to the origin may be considered as produced by a uniform pressure line

Neglecting for the moment the effect of Δp_2 the disturbance is effectively that due to a *pressure line on the surface of a deep stream flowing with other*wise uniform velocity the pressure line being at right angles to the direction of flow of the stream

It must be noted that the integral (54) has so far been considered and that it is valid for positive values of R For negative values of R the integral (55) must be evaluated The treatment of the latter integral proceeds in precisely the same manner and need not here be considered further except to mention that when $R \to 0$ the slope of the wave profile is continuous

The slope is in fact equal to $-\pi\beta e^{-h\beta}$ when $R = 0$ Its value and continuity are easily proved by means of the integrals

$$\int_0^\infty \frac{\cos ax}{1+x^2}\,dx = \int_0^\infty \frac{x \sin ax}{1+x^2}\,dx = \frac{\pi}{2}e^{-a}$$

In Lamb's Hydrodynamics an interesting drawing is given of the wave profile due to a uniform pressure distributed over a band of finite breadth but the discontinuities at the edges make this mode of representation a little unnatural

In fig 2 a diagram is shown of the wave profile due to a diffused pressure taking $h\beta = 0\cdot 1$ in formulæ (55) (57) and (61) The line OX lies on the undisturbed surface and in the direction of the flow of the stream It is legitimate to employ either (57) or (61) to the point given by $R\beta = \frac{1}{2}$ but it must be noted that the approximation given by the latter formula cannot be used with reasonable accuracy for values less than this

Notwithstanding the discrepancy due to using the one formula for the other does not amount even at this point to more than three per cent of the approximate value

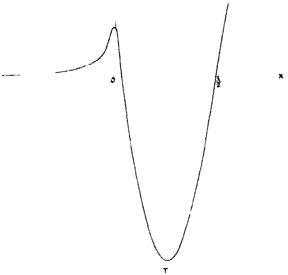

Fig 2

The line TT is the line of troughs at a sufficient distance

It will be seen then that at a short distance down stream the sine term only is sensible

In the case of a line of pressure at right angles to the shore the total effect at a short distance down stream is barring a constant factor given by

$$-2\pi e^{-k\beta}\sin R\beta\{1-2e^{-\sqrt{3}/2\,y\beta}\}$$

There is accordingly a nodal line parallel to the shore at a distance given by

$$\sqrt{3}/2\ y\beta=\log_e 2$$

or

$$y=0.127\,\lambda$$

(*See* Lamb's Hydrodynamics 4th Ed p 443)

A Pressure Point —When the applied pressure is symmetrical about a point it is necessary to return to equations (52) and (53) Remembering that

$R = r\cos(\phi-\theta)$, where r is the distance from this point the most important part of ζ_1 is given by

$$\zeta_1 = -\frac{P}{\rho\pi}\int_{-\pi/2}^{+\pi/2} 2\pi\beta \sin\left\{\frac{r\cos(\phi-\theta)g}{c^2\cos^2\phi} - \epsilon\right\}\frac{d\phi}{c^2\cos^2\phi}e^{h\beta} \qquad (62)$$

Since $\tan\epsilon = 4\sin\phi/\sqrt{3}\cos^2\phi$ it can be shown easily that the integral is convergent

The most important part of this integral is obtained from the group of values of the integrand lying in the neighbourhood of that value of the harmonic argument for which the phase remains stationary Write therefore

$$F = \frac{rg}{c^2}\frac{\cos(\phi-\theta)}{\cos^2\phi} - \epsilon \qquad (63)$$

and put $\tan\epsilon = A\sin\phi/\cos^2\phi$ (A being written for $4/\sqrt{3}$)

The condition for stationary phase is $\partial F/\partial\phi = 0$ which leads to

$$[x_0u + y_0(2u^2+1)][1 + A^2u^2 + A^2u^4] = 2u^2+1 \qquad (64)$$

in which

$$u = \tan\phi$$

and

$$x_0 = rg\cos\theta/Ac^2$$

$$y_0 = rg\sin\theta/Ac^2$$

Along the curves of cusps $\partial^2 F/\partial\phi^2$ must vanish

This condition leads to the equation

$$\{x_0 + y_0 4u\}\{1 + A^2u^2 + A^2u^4\} + \{x_0u + y_0(2u^2+1)\}\{2u^2+1\}2A^2u - 4u \qquad (65)$$

Write for brevity

$$B = 1 + A^2u^2 + A^2u^4$$

$$C = \frac{2A^2u^2(2u^2+1)^2}{2u^2-1}$$

then from (64) and (65)

$$\left.\begin{aligned} x_0 &= \frac{C}{B^2}\,\frac{2u^2+1}{u} \\ y_0 &= \frac{1}{B} - \frac{C}{B^2} \end{aligned}\right\} \qquad (66)$$

When $u \to \infty$, both x_0 and y_0 are zero

When $u = 0$, $x_0 = 0$ and $y_0 = 1$

When $u = \pm 1/\sqrt{2}$ both x_0 and y_0 are infinite

Now

$$\frac{y_0 - 1/8}{x_0} = -\frac{u}{2u^2 + 1} \tag{67}$$

and the asymptotes to the curves of cusps are given by putting $u = \pm 1/\sqrt{2}$ in (67) Thus the equations of the asymptotes are

$$y_0 - \tfrac{1}{8} = \mp \frac{1}{2\sqrt{2}} x_0$$

The scale of x_0 and y_0 is to be interpreted from the relation

$$Ac^2/g = A\lambda_0/2\pi$$

where λ_0 is the length of the free waves upon a stream of infinite depth flowing with velocity c

In fig 3 is presented a diagram of the cusp curves OC O B showing the asymptotes AB and AC The curves are derived from equations (66)

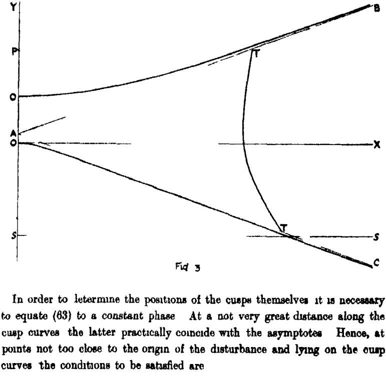

Fig 3

In order to determine the positions of the cusps themselves it is necessary to equate (63) to a constant phase At a not very great distance along the cusp curves the latter practically coincide with the asymptotes Hence, at points not too close to the origin of the disturbance and lying on the cusp curves the conditions to be satisfied are

From (63)

Also

corresponding to

$$\left.\begin{aligned} \frac{Ax_0\cos\phi + Ay_0\sin\phi}{\cos^2\phi} - \epsilon &= 2n\pi \\ y_0 - \tfrac{1}{8} &= \mp\frac{x_0}{2\sqrt{2}} \\ \tan\phi &= \pm 1/\sqrt{2} \end{aligned}\right\} \qquad (68)$$

If s be the distance along the asymptotes from A (fig 3),

$$y_0 - 1/5 = \mp s/3$$

$$x = 2\sqrt{2}\,s/3$$

corresponding to $\tan\phi = \pm 1/\sqrt{2}$

Taking first $\tan\phi = +1/\sqrt{2}$ it follows that along the asymptote AC

$$2s - 2\sqrt{3}\tan^{-1}2 = 2n\pi$$

Similarly, along the asymptote AB

$$2s - 2\sqrt{3}\tan^{-1}2 = 2n\pi$$

Along the axis OX s is approximately equal to $\sqrt{3}/2 \cdot n\pi$. In fig 3 the curve TT represents a nodal line of the transverse wave system obtained by means of the first of equations (68) combined with the first of (64)

The effect of Δp_2 may be treated in the same way but the following observations will suffice

Instead of (63) the required phase function is

$$F = \frac{rg}{c^2}\frac{\cos(\phi - \theta)}{\cos\phi} + \gamma \qquad (69)$$

in which $2\sin\gamma = \sin\epsilon$

It will be observed from (50) that $y - a$ is replaced by $y - 2a$. The initial disturbance exists at the point $x = 0$, $y = 2a$ and the asymptotes to the cusp curves make angles $\pm\theta_0$ with the axis of x where again $\tan\theta_0 = 1/2\sqrt{2}$

Owing to the presence of the factor M Δp_2 produces a sensible effect only close to the edge of the shore. In order to investigate the nature of the motion close to the shore, the positions of the cusps may be determined. For it can be shown that

$$\frac{\partial\gamma}{\partial\phi} = \frac{1}{2}\,\frac{1}{2n^2+1}\,\frac{\partial\epsilon}{\partial\phi}$$

The asymptotes pass through the point P (0, 2a) (fig 3) and make the angle stated with the axis of x

The transverse waves, which of course exist only near the shore, can be drawn in as before It is sufficient to remark that, since γ is opposite in sign to ϵ, the orientation of these waves with respect to the central line is opposite to that of the transverse waves of which a member is depicted in fig 3.

The Case $\theta_0 = -45°$ —This problem will be considered briefly for the analysis is in many respects, similar to the foregoing

From equation (43) for the velocity potential of simple harmonic motion there is derived

$$\phi_1 = A\left[\cos\epsilon\ e^{-\lambda y} + \cos(\mu y - \epsilon)\right] \tag{70}$$

Equation (70) shows that, in contradistinction to the previous case when $\theta_0 = -30°$, no motion is possible in which there is a single nodal line parallel to the edge of the shore For when $\mu = 0$, $\epsilon = -\pi/2$, so that $\phi_1 = 0$ For other values of μ or ϵ the nodal lines, after the first, are practically determined by the equation

$$\cos(\mu y - \epsilon) = 0$$

Multiply ϕ_1 by the factor $2\cos\mu a$ Then

$$\left.\begin{aligned}\frac{2\cos\mu a}{A}\ \phi_1 = 1 &\quad \cos\{\mu(y-a) - \epsilon\}\\ 2 &\ + \cos\{\mu(y+a) - \epsilon\}\\ 3 &\ + \cos\{-\mu a - \epsilon\}\, e^{\lambda y}\\ 4 &\ + \cos\{\mu a - \epsilon\}\, e^{-\lambda y}\end{aligned}\right\} \tag{71}$$

The term (1) of (71) gives rise to an equation similar to (51), with the only difference that now

$$\cot\epsilon = -\sin\phi$$

The wave pattern due to the first term of (71) is derived from a consideration of the phase function

$$F = \frac{rg}{c^2}\,\frac{\cos(\phi - \theta)}{\cos^2\phi} - \epsilon$$

Let

$$x_0 = rg\cos\theta/c^2, \qquad y_0 = rg\sin\theta/c^2,$$
$$u = \tan\phi, \qquad B = 1 + 2u^2$$

Then it can be shown that the cusp curves are obtained from the equations

$$\left.\begin{aligned} x_0 u + y_0 B &= 1/B\\ x_0 + y_0\ 4u &= -4u/B^2\end{aligned}\right\}, \tag{72}$$

from which it appears that the asymptotes to these curves again make angles $\pm\tan^{-1} 1/2\sqrt{2}$ with the axis of x

The interest of these problems lies largely in the contrast which they present to the problem of uniform finite depth

Consider now the third term of (71) On referring to equation (51) the only modifications required are that h should be replaced by $h + y$, and that $y - a$ should be replaced by $-a$ Hence r and θ must be interpreted as

$$r \cos \theta = x,$$

$$r \sin \theta = -a$$

The asymptotes are given by the same values of θ, and it is obvious that the effective disturbance due to this term exists beyond the point where the near asymptote cuts the edge of the shore, and is, along the edge of the shore, of the same magnitude and sign as pertain to that due to the first term

It is of interest to treat this problem somewhat further

Write $2n\pi + \frac{1}{2}\pi = C$, where n is an integer, and let

$$\frac{g}{c^2} \frac{x}{\cos \phi} + \frac{g}{c^2} \frac{y \sin \phi}{\cos^2 \phi} - \epsilon = C$$

Let

$$A = \cos \phi \{C - \cot^{-1} (\sin \phi)\}$$

It is, then, not difficult to show that the crest curve, corresponding to some constant value of n, is given by the equations

$$\frac{gx}{c^2} = A \frac{1 + 2u^2}{1 + u^2} - \frac{u}{(1 + u^2)(1 + 2u^2)},$$

$$\frac{gy}{c^2} = \frac{1}{(1 + u^2)(1 + 2u^2)} - \frac{u}{1 + u^2} A,$$

where $u = \tan \phi$

When u is small and C moderately large

$$\frac{y}{x} = \tan \theta = \frac{1}{A} - u \text{ approximately}$$

Hence, for small values of u and integral values of n, θ is small It thus follows that, for small values of θ, the principal wave groups which contribute to the transverse wave system are determined by small values of ϕ

The potential function

$$\cos \epsilon \quad e^{\lambda y} + \cos (\mu y - \epsilon)$$

may be treated in the same manner as that adopted for the case of a shore inclined at 30° to the horizontal It is unnecessary to go through the work in detail but it can be shown that, if $g/c^2 \cos\phi = \kappa$, the surface elevation required is proportional to ζ, where

$$-\zeta = \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} \frac{d\phi}{\kappa} \sin\left[\kappa\left\{x\cos\phi + (y-a)\sin\phi\right\} - \epsilon\right], \tag{A}$$

$$+ \text{ a similar term obtained by substitution } y+a \text{ for } y-a, \tag{B}$$

$$+ \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} \frac{d\phi}{\kappa} e^{-\kappa y} \sin\left[\kappa\left\{x\cos\phi + a\sin\phi\right\} - \epsilon\right] \tag{C}$$

$$+ \text{ a similar term obtained by substituting } -a \text{ for } +a \tag{D}$$

The group method is now used to determine the most important part of the integral (A) Denoting the argument of the sine term in (A), by F, it is found that, for small values of ϕ

$$F = \kappa\left\{x\left(1 + \tfrac{1}{2}\phi^2\right) + (y-a)\phi\right\} + \frac{\pi}{2} - \phi$$

The condition $\partial F/\partial\phi = 0$ leads to

$$\kappa\left\{x\phi + (y-a)\right\} - 1 = 0,$$

whence

$$F = \kappa x - \frac{\left\{\kappa(y-a) - 1\right\}^2}{2\kappa x} + \tfrac{1}{2}\pi$$

At points close to the axis of x, the chief difference between this case and the case of infinite depth lies in the fact that in the former

$$\zeta \propto \cos\left(\kappa x + \tfrac{1}{4}\pi\right),$$

and in the latter

$$\zeta \propto \cos\left(\kappa x - \tfrac{1}{4}\pi\right)$$

The difference between the forms found for the crest curves near the axis may also be noted

The diminution of amplitude in proportion to $x^{-\frac{1}{2}}$ is practically unaltered At points on the surface of the stream, below that at which the cusp curve due to (A) cuts the edge of the shore, an approximation to the four integrals (A, B, C, D) can now be written down At points close to the shore all four integrals are sensible, but at a short distance from the shore the two last become negligible The phenomenon is easily observed when navigating a motor boat in shallow seas On steering close up to a sloping shore the transverse waves on the port side rapidly increase in height The explanation is, of course, readily given in general terms, but the working out of an actual case in which the problem can be rigidly formulated has been of interest since the opportunity offered itself of observing the phenomenon on several occasions while on holiday last summer

5 SHIP WAVES ON A SEA OF UNIFORM FINITE DEPTH

In the first place consideration must be given to the integrals obtained in the second section

In equation (32) since $\sum_1^\infty$ is common to all cases it will have first treatment

When considering the lowest imaginary root the suffix n will be dropped as has been done in the case of the real root since no confusion can be caused now

Now

$$\pi i \frac{F(iv_n)}{f(iv_n)} \qquad \frac{\pi v_n L e^{Rv_n \quad ihv_n}}{\{v_n^2 - L(1-L)\}} \tag{73}$$

and the sum required is

$$S_\infty \qquad \sum^{\infty} \frac{\pi e^{Rv_n} \cos hv_n}{v_n/L + L/v_n - 1/v_n} \tag{74}$$

The series (74) has some properties which should be noted The lowest possible value of v_n is π and whatever the values of L and v_n the minimum value of $v_n/L + L/v_n$ is 2 It can be easily shown that if h is finite however small the series is convergent for all values of R In the present discussion h is considered to be small For given values of R and h the sum will depend upon the magnitude of L The maximum value of the sum will occur when L lies in the neighbourhood of the lowest value of v_n and complying also with the condition

$$v_n = L \tan v_n$$

Thus the sum of the series will be a maximum when L lies between π and $5\pi/4$ When L is either very great or very small the sum of the series approaches zero

For values of L which are less than unity it is possible to find a close approximation to the sum of the series From the foregoing observations it is legitimate to omit $1/v_n$ from the denominator of (74) If this be done the n^{th} term of the series may be written approximately —

$$\tfrac{1}{2}\pi e^{Rv} \cos hv_n \sin 2v_n \tag{75}$$

Now

$$v_n = (2n+1)\tfrac{1}{2}\pi \qquad \epsilon$$

in which, for all integral values of n, ϵ may be considered small. Thus $\sin 2v_n$ is approximately equal to $2L/(2n+1)\frac{1}{2}\pi$ Thus the n^{th} term may be written approximately

$$\pi e^{-R\epsilon_n} \cos hv'_n \; L/v'_n,$$

where

$$v'_n = (2n+1)\tfrac{1}{2}\pi$$

It follows that

$$\begin{aligned} \partial S_\infty/\partial R &= \text{the real part of } -\pi L\Sigma e^{(-R+ih)v'_n} \\ &= \text{the real part of } -\pi L\frac{e^{\frac{1}{2}(-R+ih)\pi}}{1-e^{(-R+ih)\pi}} \end{aligned}$$

When R is small (h being assumed small throughout)

$$\partial S_\infty/\partial R = -\frac{RL}{R^2+h^2} \text{ approximately}$$

If x be written for $e^{-\frac{1}{2}\pi R}\cos h\frac{1}{2}\pi$, where h is small, an approximation to S_∞, for values of $L<1$, is given by

$$L\left\{\log\frac{1+x}{1-x}-2x\right\}. \tag{76}$$

The validity of this expression for small values of R will be discussed presently

The contribution which the series just considered makes to ζ is very small except for very small values of R and produces no wave pattern It is convenient, henceforth, to denote g/σ^2 by κ

The important integrals, which remain, have now to be considered. These are involved in the equation

$$\frac{\rho\pi g}{P}\frac{\partial\zeta}{\partial\phi} = 2\pi i\frac{F(u)}{f'(u)} + \pi i\frac{F(iv)}{f'(iv)}, \tag{77}$$

ζ being that part of the surface elevation due to these terms, and it being understood that only the real parts are retained The first part of the right hand side of (77) applies to those values of ϕ for which $L>1$ and R positive The second part applies to those values for which $L<1$, and, remembering the statement made in the second section, it applies whether R be positive or negative

Consider, in the first place, the second part, viz —

$$\frac{\rho\pi g}{P}\frac{\partial\zeta}{\partial\phi} = \frac{\pi e^{-Rv-ivh}}{\tan v+\cot v-1/v} \tag{78}$$

The right hand side of (78) is infinite when $v=0$, so that, in the case of the two-dimensional problem when ϕ is zero, the solution is indeterminate when κ

is exactly equal to unity It is, of course, then necessary to take account of a finite frictional resistance between the particles of the fluid This was referred to above

A pressure Line when $\kappa < 1$ —Before proceeding further, it may be noted that equations (76) and (78) contain the solution of the two-dimensional problem in which κ is less than unity, κ being written for L

The validity of the expression (76) for small values of R must, however, be considered It will be noted that $\partial S_\infty/\partial R = 0$ when $R = 0$, but the derivative of (78) with respect to R is not zero when $R = 0$ The sum of these expressions does not, therefore, satisfy the condition that the slope is zero when $R = 0$

In fact the series from which $\partial S_\infty/\partial R$ is obtained becomes indeterminate when $R = 0$

The whole expression may, however, be transformed by (28) into the integral

$$I = \int_0^\infty \frac{\kappa\, du \cos(Ru)\, e^{-hu}}{u \coth u - \kappa}, \tag{79}$$

which shows that $\partial I/\partial R = 0$ when $R = 0$

Transform the equation for $\partial S_\infty/\partial R$, when R is small, into

$$\frac{\partial S'_\infty}{\partial R} = -\frac{(R+\alpha)\kappa}{(R+\alpha)^2 + h^2},$$

in which α may be considered as very small

When R is zero this becomes

$$\frac{\partial S'_\infty}{\partial R} = -\frac{\alpha\kappa}{\alpha^2 + h^2} \tag{80}$$

The derivative of the real part of (78) with respect to R, when $R = 0$, is

$$-\frac{\pi v \cos hv}{\tan v + \cot v - 1/v},$$

which has a given value, A say, when κ is given

Hence it is necessary to equate

$$\frac{\alpha\kappa}{\alpha^2 + h^2} \text{ to } -A,$$

or, since α is very small,

$$\alpha = -Ah^2/\kappa$$

Now, for small values of R,

$$S'_\infty = \log\{(R+\alpha)^2 + h^2\}^{-\frac{1}{2}}, \tag{81}$$

which shows that S'_∞ may be substituted for S_∞ when $R = 0$, and when $R > h$, since α is small compared with h Between these values of R, S'_∞ and (78) together are a valid representative of the profile as far as the second power of R, for the first power disappears If, therefore, $R - Ah^2/\kappa$ be substituted for R in (76), the latter, together with (78), may be used to delineate the whole profile

In fig 4 is depicted the profile for a value of $\kappa = \pi/4$, and $\cos(h\frac{1}{2}\pi) = 0\ 9$ In this case $v = \kappa$ and

$$\tan v + \cot v - 1/v = 2 - 4/\pi$$

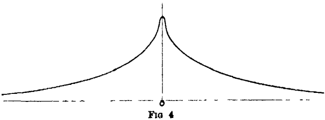

Fig 4

A Pressure Point —The most important part of the wave disturbance is due to the first term on the right hand side of (77), when modified to suit the pressure distribution given by (9)

This term may then be written

$$\frac{\rho\pi g}{P}\ \frac{\partial\zeta}{\partial\phi} = 2\pi i\,\frac{u^2 L e^{iRu}}{\{L(1-L)+u^2\}}, \tag{82}$$

where $u = L \tanh u$

The damping factor h has been omitted, for it is unnecessary to retain it in the subsequent investigations In the remainder of this problem ζ denotes that part of the surface elevation due to the term under consideration

Let the factor

$$u^2L/\{L(1-L)+u^2\}, \quad = u/\{\tanh u - \coth u + 1/u\},$$

be denoted by B

Then

$$\frac{\rho\pi g}{P}\ \frac{\partial\zeta}{\partial\phi} = -2\pi B \sin(Ru). \tag{83}$$

The value of ζ at any point may now be considered as due to the superposition of an infinite number of elements $\delta\phi$ At a given point the most important part of the integral with respect of ϕ arises from those values of ϕ which lie in the neighbourhood of ϕ_0, where ϕ_0 is such as to make the argument of the circular function stationary For a given value of ϕ, say ϕ_0, if the applied pressure be confined to the neighbourhood of the line ϕ_0, the motion is practically two-dimensional, and, at a moderate distance along the perpendicular to the line, in the direction of the resolved flow of the stream, the form of the free surface is given by the right hand side of (83) Except, therefore, at points close to the origin, each element $\delta\phi$ produces a stationary wave form whose wave length depends upon ϕ Now, by an application of the group method, to each value of θ corresponds a value of ϕ Lines may be drawn parallel to this value of ϕ at perpendicular distances given by

$$\mathrm{R}u = (2n+1)\pi + \tfrac{1}{4}\pi,$$

where u corresponds to the said value of ϕ Where these lines cut θ, the predominant elevations will be situated

The Wave Profile

With regard to the amplitudes of the wave pattern the group method can be used, but since the harmonic wave form produced by an element $\delta\phi$ is not established very near this element, the theory does not apply to points close to the origin

From (83) it follows that

$$\frac{\rho n g}{\mathrm{P}}\zeta = -\int 2\pi\mathrm{B}\sin\{r\cos(\phi-\theta)u\}\,d\phi \tag{84}$$

Denote $r\cos(\phi-0)u$ by F, and consider F as a function of ϕ, r and θ being given The most important part of the integral (84) comes from a small range of values of ϕ lying in the neighbourhood of some value ϕ_0, which is given by the equation $\partial\mathrm{F}/\partial\phi = 0$

In the neighbourhood of ϕ_0 the function F is given approximately by a few terms of the series

$$\mathrm{F} = \mathrm{F}_0 + \left[\frac{\partial\mathrm{F}}{\partial\phi}\right]_0(\phi-\phi_0) + \tfrac{1}{2}\left[\frac{\partial^2\mathrm{F}}{\partial\phi^2}\right]_0(\phi-\phi_0)^2 + \tag{85}$$

It is easily shown that an approximation to ζ is then given by

$$\frac{\rho g}{\mathrm{P}}\zeta = -2\sqrt{2\pi}\;\mathrm{B}\left[\frac{\partial^2\mathrm{F}}{\partial\phi^2}\right]_0^{-\frac{1}{2}}\cos\{\mathrm{F}_0 \mp \tfrac{1}{4}\pi\}, \tag{86}$$

the upper sign being taken when $[\partial^2\mathrm{F}/\partial\phi^2]_0$ is positive and the lower sign when it is negative. If $[\partial^2\mathrm{F}/\partial\phi^2]_0$ is also zero, it is necessary to proceed to the third term in the development of F in order to find the approximate value of the integral.

Considering now the application of (86) it is not difficult to show that

$$-2\sec^2\phi = (\alpha - 1)\frac{1}{u}\frac{\partial^2 u}{\partial\phi^2} + \left(\frac{1}{u}\frac{\partial u}{\partial\phi}\right)^2\left(1 - \frac{2\alpha}{\beta} + \alpha^2\right), \tag{87}$$

where

$$\cos^2\phi = \kappa \tanh u/u = \kappa\beta, \text{ say},$$

and

$$2u/\sinh 2u = \alpha$$

The derivatives of F obviously become rather complicated in their general form The most important case is concerned with the transverse waves along the line $\theta = 0$ When $\theta = 0$, $\phi = 0$, and from (87) it follows that

$$\frac{\partial^2 F}{\partial\phi^2} = ru\frac{1+\alpha}{1-\alpha},$$

the required value of u being given by

$$\tanh u/u = 1/\kappa$$

It may be noted that, when $\kappa = 1$, $u \to 0$, and $\partial^2 F/\partial\phi^2$ is then infinite Also when κ is large, $u \longrightarrow \kappa$, and $\partial^2 F/\partial\phi^2 \longrightarrow r\kappa$ The complete expression for the vertical section of the transverse wave system, along the line $\theta = 0$, is now given by

$$\frac{\rho g}{P}\zeta = -\frac{2u}{C}\left(\frac{2\pi}{r}\right)^{\frac{1}{2}}\cos\left(ru - \tfrac{1}{4}\pi\right), \tag{88}$$

where

$$C = \left(\frac{1-\alpha^2}{u}\right)^{\frac{1}{2}}$$

When κ is moderately large

$$C \longrightarrow \text{the value } u^{-\frac{1}{2}} \text{ or } \kappa^{-\frac{1}{2}}$$

When κ is nearly equal to unity, so that u is small,

$$C \longrightarrow \text{the value } 2\left(\frac{\kappa - 1}{3\kappa}\right)^{\frac{1}{2}}$$

When κ is equal to unity, the failure of the solution is due to the neglect of the frictional resistance between the particles of the fluid, and the solution is indeterminate, therefore, unless some such resistance is assumed to be present

It may be pointed out here that, when $\kappa < 1$, the boundary lines of the wave pattern coincide with those values of ϕ given by $\pm\cos^{-1}(\kappa^{\frac{1}{2}})$ Since these lines are themselves the origins of the chief dispersive wave groups at points lying in their own vicinity, no quantitative conclusion concerning the disturbance at the boundaries can be drawn by an application of the group method

A general expression for the surface form along the lines of cusps can be obtained for values of $\kappa > 1$, but it is complicated When $\kappa < 1$ the boundary lines of the wave pattern are not cuspidal lines, and the determination of the surface form along these boundary lines is not possible by the preceding methods for the reasons already stated At points well within the boundary lines these methods may, however, be used It may be noted that, when $\kappa > 1$, as passage is made from any one of the crests of the transverse wave system through a cusp to the corresponding crest of the diverging wave system, since $[\partial^2F/\partial\phi^2]_0$ is zero at the cusp, it changes sign, and therefore the phase changes sign on passing through a cusp When κ is large the wave form along the lines of cusps is readily obtained For in this case

$$\kappa = u\cos^2\phi, \quad B = u^2, \tag{89A}$$

and

$$F\cos^2\phi = \kappa r\cos(\phi - \theta) \tag{89B}$$

Since $\partial F/\partial\phi = 0$ and $\partial^2F/\partial\phi^2 = 0$, successive differentiation of (89B) gives

$$1 \quad \tan(\phi - \theta) = 2\tan\phi,$$

an equation already obtained,

$$\left.\begin{array}{l} 2 \quad 3\cos^2\phi = 2, \quad \text{whence } B = (3\kappa/2)^2, \\ 3 \quad \partial^3F/\partial\phi^3 = -3\kappa r\sqrt{\tfrac{8}{3}} \end{array}\right\} \tag{90}$$

It follows that

$$-\frac{\rho g}{P}\zeta = \frac{3\kappa^2}{2}\{\tfrac{1}{2}\sqrt{\tfrac{2}{3}}\,\kappa r\}^{-\frac{1}{3}}\Gamma(\tfrac{1}{3})\sin\frac{\pi}{3}\sin\left(\frac{\sqrt{3}}{2}\,\kappa r\right) \tag{91}$$

The amplitude along the cuspidal lines decreases, therefore, reciprocally as the cube root of r

6 TWO FLUIDS OF DIFFERENT DENSITY

There are some interesting phenomena connected with the wave formation due to a ship moving on the upper surface of two fluids of different density which are superposed upon one another with, in the undisturbed state, a horizontal surface of separation * Let the depth of the upper fluid be taken as unity, and let that of the lower fluid be very great Then (*see* Lamb's 'Hydrodynamics," 4th Ed , p 408), a pressure line, at right angles to the flow of the stream, will produce two wave systems

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* See Ekman, "On Dead Water," 'Scientific Results of the Norwegian North Polar Expedition,' Part XV, Christiania, 1904

The wave lengths of the two systems are, respectively, given by

$$\kappa_1 = g/c^2 \tag{92}$$

and

$$\kappa_2 = \frac{g}{c^2} \frac{\rho - \rho'}{\rho \coth \kappa_2 + \rho'}, \tag{93}$$

in which the accented letters refer to the upper fluid

The ratio of the amplitude at the upper surface to that at the surface of separation is, in the case of the first system, e^{κ_1} In the case of the second system this ratio is

$$-\frac{\rho - \rho'}{\rho'} e^{-\kappa_2} \tag{94}$$

The ship waves of the first system, which are formed at the upper surfaces are identical with those formed upon the surface of a deep sea of uniform density At the surface of separation very much the more important system is that corresponding to (93) and this system may be of considerable amplitude The wave pattern of this system is, however, somewhat restricted For the three dimensional case of ship waves the equation (93) is written in the form

$$\kappa_2 = \frac{g}{c^2 \cos^2 \phi} \frac{\rho - \rho'}{\rho \coth \kappa_2 + \rho'}, \tag{95}$$

and the phase function to be considered

$$\cos(\phi - \theta)\, \kappa_2 \tag{96}$$

The difference in density will be assumed to be small, and will be denoted by $\Delta\rho$

In accordance with the previous notation let $\kappa_2 = u$ and let $\kappa = g\Delta\rho/c^2\rho$. Then (95) becomes

$$\left.\begin{aligned} \cos^2\phi &= \kappa/u\,(1 + \coth u) \\ &= \kappa\,(1 - e^{-2u})/2u \\ &= \kappa\beta, \text{ say} \\ \text{Let } \mathrm{F} &= \cos(\phi - \theta)\, u \end{aligned}\right\} \tag{97}$$

The required stationary condition is satisfied if $\partial\mathrm{F}/\partial\phi = 0$, whence

$$\tan(\phi - \theta) = \partial u/u\partial\phi = q, \text{ say} \tag{98}$$

From this equation it follows at once that

$$\tan\theta = \frac{\tan\phi - q}{1 + q\tan\phi} \tag{99}$$

Denote $\frac{2u}{e^{2u} - 1}$ by α, then the differentiation of the equation, $\cos^2 \phi = \kappa\beta$, leads to the equation

$$-2 \tan \phi = (\alpha - 1) q \tag{100}$$

For the moment write $2/(1 - \alpha) = x$

The elimination of q from (99) and (100) results in the equation

$$\tan \theta = \frac{\tan \phi (1 - x)}{1 + x \tan^2 \phi},$$

which is readily transformed into

$$\cos^2 \theta = \frac{\{2 - (1 + \alpha) \beta\kappa\}^2}{4 - (1 + \alpha)(3 - \alpha) \beta\kappa} \tag{101}$$

The Wave Pattern

For a given value of u the limiting value of θ is found by obtaining the differential coefficient of the right hand side of (101) with respect to κ and equating it to zero

This leads to the equation

$$\beta\kappa = 2/(3 - \alpha) \tag{102}$$

Hence, from (101) at the limiting value

$$\cos^2 \theta = \frac{8(1 - \alpha)}{(3 - \alpha)^2} \tag{103}$$

$\kappa > 1$ —Since the greatest possible value of $(3-\alpha)\beta$ is 2 it follows from (102) that κ must be greater than unity when a real limiting value exists There is only one real limiting value, as an inspection of the functions β and α in (102) will show, and its existence indicates that, for given values of θ and κ in equation (101) there must be two values of ϕ, so that there are two sets of waves given by those values of ϕ which produce the predominant group values along the line $\theta =$ const

$\kappa < 1$ —There is no real limiting value in the above sense, and one of the groups disappears The limit of θ occurs in this case always when $u = 0$ If θ be made zero in (101), that equation reduces to $\beta\kappa = 1$

Now β is always less than 1, so that, when θ is zero, κ must be greater than 1 Hence the transverse waves disappear when $\kappa < 1$ When $\kappa < 1$, those values of ϕ which produce the diverging waves within the boundary lines, lie between $\pm\frac{1}{2}\pi$ and $\pm \cos^{-1} \kappa^{\frac{1}{2}}$ Those values of ϕ, lying between 0 and $\pm$

$\cos^{-1}\kappa^{\frac{1}{2}}$, are responsible for the approximate elevation given by (81) The reason for the disappearance of the transverse waves is now clear

The deduction of the preceding results is made clearer by the following considerations

Write f for $\cos^2\theta$ in equation (101) Construct two rectangular axes Of and Ou, f being a function of u, and let AB be a line parallel to the positive half of the axis of u, at distance unity from it, and cutting Of in A Then the whole available part of the function f must be contained within uOAB If $f = 1$, then $\kappa\beta = 1$, as has been seen

$\kappa > 1$ —When u is infinite, f is unity When u is given by $\kappa\beta = 1$, f is again unity Between these values of u the function f has a minimum, which has been denoted above as the real limiting value Any line $f =$ const, which lies between unity and this minimum value cuts the curve connecting f and u in two real points These two real points determine the values of u, and therefore of ϕ, corresponding to the given value of θ

$\kappa < 1$ —The curves connecting f and u have each a minimum ordinate at $u = 0$, and the value of f there is given by

$$f = 1 - \kappa$$

The boundary lines, which are the loci of the cusps of the wave pattern when $\kappa > 1$, are given by (103) When κ is large, $\alpha \to$ zero, so that the angle contained between the two lines of cusps cannot be less than $2\theta_0$, where

$$\cos^2\theta_0 = 8/9 \tag{104}$$

As κ decreases to unity, the angle $2\theta_0$ increases to π, but for further decrease of κ the angle between the boundary lines decreases to zero as $\kappa \to$ zero

The similarity between this problem and that of ship waves on a sea of uniform finite depth may be noted The latter has been dealt with in a different manner by Havelock ('Roy Soc Proc,' Series A, vol 81, p 398).

Unless c be very small, κ will be less than unity and there will be no transverse wave system The divergent wave system will be contained within two lines radiating from the origin to the rear, the angle between which will diminish as c increases

For a given value of u the ratio of the amplitude at the surface of separation to that at the upper surface is, from (94),

$$-\rho e^{u}/\Delta\rho$$

Along the boundary lines of the wave pattern $u = 0$ when $\kappa < 1$ Hence the amplitude increases rapidly for other parts of the wave pattern, as compared with that of the corresponding system at the upper surface

When c is very small, so that κ is greater than unity, $u > 0$ at all parts of the wave pattern including the boundary lines

The amplitude of the waves at the surface of separation may, in this case, assume large proportions, and to this cause has been ascribed the abnormal resistance experienced by ships near the mouths of the Norwegian fjords, where there is a layer of fresh water over salt water

The Distortion of Crystals of Aluminium under Compression.— *Part* I

By G I Taylor, F R S, and W S Farren, M A

(Received April 26, 1926)

In previous experiments on the distortion of aluminium crystals* a uniform bar was cut from a single crystal and subjected to a tension along its length This form of test ensures a uniform stress in the central part of the bar, and it was found that the distortion was uniform, and that it conformed to very simple laws These laws may be summarised as follows —

(*a*) The distortion is due to slipping, or shearing, parallel to one octahedral (111), plane in the direction of a diad axis (110)

(*b*) Of the twelve crystallographically similar possible types of slipping, in general only one occurs, namely, the one for which the component of shear stress in the direction of shear is the greatest.

It will be noticed that these laws take no account of any possible effect due to the component of pressure normal to the slip plane In the case of a tensile test there is always a tension perpendicular to the slip plane, and the question naturally arises whether the distortion would follow the same laws if the component of stress perpendicular to the slip plane were compressive The experiments described below were designed partly to give information on this point, but chiefly to find out whether the simple laws found for the distortion due to stretching are applicable to other kinds of plastic strain The chief difficulty lay in devising a kind of experiment in which the stress might be expected to be uniformly distributed through the material So far as we are aware there is no form of test known to engineers which gives a uniform plastic strain to a material except the extension of a uniform bar In torsion tests, for instance, the stress is not uniform, even when applied to isotropic materials, and when a bar cut from a single crystal is twisted the stresses must be very complicated

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* "The Distortion of an Aluminium Crystal during a Tensile Test," G I Taylor and C. F Elam, Bakerian Lecture, 'Roy Soc Proc,' A, 1923, p 643, referred to as B L. in future, and "The Plastic Extension and Fracture of Aluminium Crystals," G I Taylor and C. F. Elam, 'Roy Soc. Proc,' A, 1925, p 28, referred to as P E in future

The known type of distortion which most nearly approaches the desired conditions occurs in the ordinary compression tests used by engineers In these tests short cylindrical lengths of the material are compressed between parallel plates The distortion is not uniform, for the compressed material usually assumes a barrel-shaped form, and in any case tests of this kind are unsuitable for single crystals because the distortion would necessarily be unsymmetrical and the distorted specimen would be of such a shape that the load could not be applied centrally The distortion would therefore cease to be uniform as soon as any appreciable distortion had occurred

This eccentricity of loading could be diminished by reducing the height of the specimen in comparison with its diameter, and if the specimen were cut in the form of a thin disc it could be made quite negligible. On the other hand, there is another factor which tends to give rise to non-uniformity of stress in the material—namely, the friction between the end plates and the specimen. It is this friction which causes the specimens used in the ordinary engineer's compression tests to become barrel-shaped. The effect of this friction in making the stresses non-uniform must be greater for thin discs than for thick ones, so that there are two factors, each tending to give rise to non-uniformity of stress The effect of one can be diminished by decreasing the height of the specimens, while the effect of the other can be diminished by increasing it In these circumstances it became a matter for experiment to find out whether, when the friction of the specimen on the end plates had been reduced as much as possible, a ratio of height to diameter could be chosen such that a cylindrical or disc-shaped specimen would be distorted uniformly under compression.

Specimens were prepared by cutting discs from single crystal bars of circular cross-sections about 1 4 cm in diameter. As it was necessary to find by means of X-ray reflections the directions of the crystal axes at various stages of the tests, special precautions were taken to ensure that the layer of material disturbed by the cutting tools should be as small as possible The cylindrical piece of material from which the disc was to be cut was set inside a brass tube and concentric with it, the annular space between them being filled with sulphur The brass tube was then mounted in a chuck in a lathe and the end faced off with a very fine cutting tool The last 6 mm of the brass tube was next turned off, leaving 6 mm of the aluminium specimen projecting from it The disc was then cut off by means of a very fine saw and the rough face trued up on a lathe with a fine tool so as to be parallel to the face already trued The specimen was next mounted on a specially designed holder and its two faces were ground down on fine emery paper stuck to a piece of plate glass The final thickness of the specimens was usually about 2 5 mm

Preliminary experiments were made with specimens prepared in this way They were pressed between parallel horizontal steel plates which had been faced in a lathe and polished with fine emery paper It was found that the circular discs became elliptic in plan In elevation or vertical section they ceased to be rectangular because the generators of the curved sides became inclined to the vertical In general, a uniform distortion would change the shape of a circular disc in this way In order to get some idea of how nearly the distortion was uniform, straight scratches were ruled on the plane faces of the specimen before compression, and these were examined afterwards to find out whether they had become bent or curved

It was found that if the specimen was not lubricated with grease distortion was far from uniform Straight scratches became curved and the specimen when seen sideways became barrel shaped and skew, as shown in Fig 1A. When the specimen was lubricated with grease both these signs of non-uniformity diminished greatly, the compressed specimen appearing as in fig 1B. Finally, the friction was still further reduced, firstly, by hardening, grinding and polishing the steel plates with diamantine powder, and secondly, by carrying out the compressions in small steps, re-greasing the specimen before each small increase in compressive load

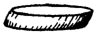

FIG 1A —Side view of specimen compressed without lubrication

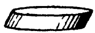

FIG 1B —Side view of specimen lubricated during compression

When tests were carried out in this way the distortion seemed quite uniform, except occasionally in a small region close to the curved edge of the specimen Photographs of one of the specimens before and after compression are shown in fig 2. The magnification of the photographs is approximately 4 5 The specimen is marked in a manner to be described presently It will be seen that straight lines* remain straight after compression and that squares ruled on the surface become oblique parallelograms

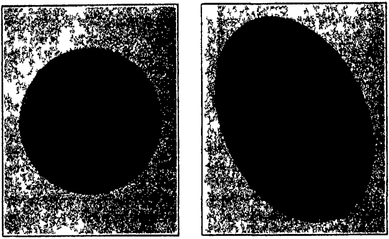

FIG 2 --Photographs of disc No. 59 10 after compression and similar disc before compression

Marking the Specimens

In order to measure the distortion and to find its relationship with the crystal axes it is necessary to rule fiducial marks on the original bar before cutting it into discs (The orientation of the crystal axes was measured with reference to these marks before the specimen was cut up) For this purpose the round single-crystal bar was mounted on V blocks on a surface plate and four generators of the cylinder were marked with a scribing block These were spaced at intervals of 90° round the specimens and numbered 1 2 3 4 A fifth generator was also ruled in such a position that the marks could be distinguished after the specimen had been cut up The bar was then cut into discs in the manner described above and cross marks were then made on the two plane faces so that the distortion could be measured

The system of marking is shown in fig 3 Two sets of three parallel lines were drawn intersecting in nine points numbered 1, 2, 3, 4, 5, 6, 7, 8, 9 The middle line of each series was ruled so that it passed approximately through a pair of opposite marked generators Thus, the line through points 2, 5, and 8 marked approximately the axial plane in the original uncut specimen which passed through the generators marked 2 and 4

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* The particular specimen shown in the photograph was marked much more deeply than those used in the experiments described below as it was found that the finer marks used in the latter specimens did not show up clearly in a photograph.

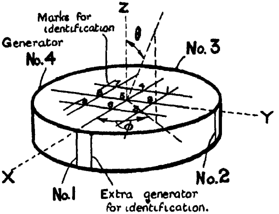


Fig 3 —System of marking and position of axes used in analysis of distortion

It was not found possible to mark the specimens satisfactorily by hand The special marking machine which is shown diagrammatically in fig 4 was

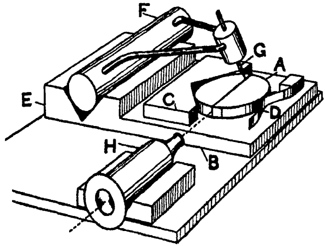


Fig 4 —Apparatus for ruling scratches

therefore constructed. In that drawing A is the specimen resting on a flat plate B and pressed against a V-groove C by a spring D A V-block E is mounted so that a cylindrical steel rod F can slide along it, and a sharpened gramophone needle G is rigidly attached to F in such a position that it passes over the centre of the specimen, scratching a straight mark.

In order to compare different discs cut from the same single crystal, it was necessary to rule the scratches so that they were always in the same orientation with respect to the marked generators on the curved surface To ensure this, a microscope H (fig 4) is mounted and focussed on the curved surface of the specimen, which is then turned round in the V-groove C till the generator marked 1 comes on to the cross-wires The microscope is fixed in such a position that its axis is parallel to the V-groove E and passes approximately through the centre of the specimen

After ruling the middle line passing through the points 4, 5, 6 (fig 3), the two parallel lines passing through points 1, 2, 3 and 7, 8, 9 were ruled For this purpose two sliders were made similar to that shown at F in fig 4, but in one the scratching-point was fixed nearer to the slider and in the other further away. To rule the three lines 1, 4, 7 , 2, 5, 8 , and 3, 6, 9, the specimen was turned in the V-groove C till the generator 2 came on the cross-wires of the microscope Scratches were then made with the three sliders used before. Further short scratches were made to assist in identifying the ruled markings These are shown in fig 3, and they can also be seen in the photographs on fig 2 After ruling the six lines on one side, the specimen was turned upside down and six similar lines were ruled on the bottom The nine points so obtained were numbered 1′, 2′, 3′, 4′, 5′, 6′, 7′, 8′, 9′, the point 1′ being approximately under point 1, 2′ under 2, etc

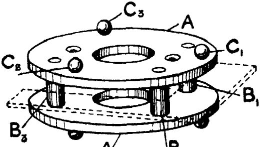
Measurement of Specimens

Having marked the specimens, such measurements were made of the relative positions of the points as were necessary to enable the distortion to be calculated For this purpose, a reading microscope was used which is capable of measuring rectangular co-ordinates on a plane

All measurements both before and after compression were reduced to the rectangular system of co-ordinate axes ox, oy, oz, shown in fig 3 The origin is the point 5 in the upper face , ox lies along the line 4, 5, 6 , oy is perpendicular to it, so that before distortion oy nearly coincides with the line 2, 5, 8. z is measured upwards perpendicular to the face, so that if t represents the thickness of the specimen, the z co-ordinate of all points in the lower surface is $-t$.

Assuming the distortion to be uniform, it was necessary to measure the x and y co-ordinates of points 2, 4, 5, 6, 8 on the upper surface and also the x, y, and z co-ordinates of the point 5′ on the lower surface, in order that a complete calculation of the distortion could be made Measurements of the x and y co-ordinates of points on the lower surface gave rise to some trouble, and the following method was finally adopted for making them The specimen was mounted in the holder, shown in fig 5A This consists of two brass discs A, A, rigidly fixed to one another by three steel pillars B_1, B_2, B_3 Three steel balls C_1, C_2 C_3, soldered to the top, and three similar balls to the bottom, form two alternative sets of legs which support the apparatus horizontally on the stage of the microscope either upright or upside down The specimen was mounted horizontally in the middle of the holder, and in order that the ruled scratches might still be in focus when the holder was inverted to look at the lower surface of the specimen it was necessary to mount the specimen midway between the two sets of balls C_1, C_2, C_3 For this purpose a subsidiary holder was used, consisting of two steel plates, D_1, D_2 (fig 5B), containing holes slightly smaller than the specimen, which was mounted between them so that the ruled

Fig 5A.



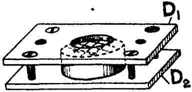


Fig 5B.

Figs 5A and 5B —Holders for use during measurement of specimen scratches could be seen through the holes This subsidiary holder was then mounted in the main holder, shown in fig 5A, and packed up with brass and paper strips till the upper face of the specimen was in focus when the holder was upright, and the underside came into focus when it was reversed

A small steel square in the form of a rectangular L is fixed to the stage of the microscope at the level of the midpoints of the pillars B_1, B_2, B_3 when the holder rests on the stage The pillars are so spaced in the holder that, when B_2 rests in the corner of the square touching both arms, B_3 and B_1 are each in contact with an arm of the square The position of the square is indicated by the dotted lines in fig 5A The square is finally adjusted so that its arms are parallel to the axes of the co-ordinate system measured by the reading-microscope

Call these co-ordinates ξ and η, and suppose the pillars B_2 and B_3 are originally in contact with the arm of the square which is parallel to the axis ξ If the holder is reversed, and B_2 and B_3 again placed in contact with the arm parallel to ξ, the displacement of the holder is equivalent to a rotation through 180° about the axis η, together with a translation parallel to the axis ξ Such a displacement leaves the η co-ordinates of all points in the holder and the specimen unaltered In this way the η co-ordinates of points on the back of the specimen relative to points on the front can be obtained Similarly, by reversing the specimen and bringing the pillars B_1, B_2 into contact with the arm of the steel square which is parallel to the axis η, the ξ co-ordinates of points on the back of the specimen relative to points on the front can be measured

It is seldom possible to mount the specimen in the holder so that the x, y co-ordinate system of the specimen is accurately parallel to the ξ, η system of the microscope The angle between them can be calculated from the measured ξ, η co-ordinates of the points 4 and 6 Thus, if this angle is w

$$\tan w = \frac{\eta_6 - \eta_4}{\xi_6 - \xi_4} \tag{1}$$

In order to check the measurements this angle was also measured by means of a microscope with a rotating eye-piece which was kindly lent us by Dr A Hutchinson, F R S At the same time the angle χ between the two sets of scratches was measured.

Calculation of Distortion

To find the nature of the distortion from the measurements made on the surface of the specimen the method previously adopted in the case of tensile test pieces* was used The unextended cone, or cone containing all the directions of lines of particles which are the same length after distortion that they were before, was found To do this the extension of the material parallel to the two sets of scratches was found If the measured ξ, η co-ordinates of the point 4 are ξ_4, η_4 before compressing, and ξ_4', η_4' after compressing, the ratio of the final distance between points 4 and 6 to the initial distance is

$$\alpha = \frac{\{(\xi_6' - \xi_4')^2 + (\eta_6' - \eta_4')^2\}^{\frac{1}{2}}}{\{(\xi_6 - \xi_4)^2 + (\eta_6 - \eta_4)^2\}^{\frac{1}{2}}} \tag{2}$$

Similarly the ratio of the final to the initial length of lines parallel to the line joining the points 2 and 8 is

$$\beta = \frac{\{(\xi_2' - \xi_8')^2 + (\eta_2' - \eta_8')^2\}^{\frac{1}{2}}}{\{(\xi_2 - \xi_8)^2 + (\eta_2 - \eta_8)^2\}^{\frac{1}{2}}} \tag{3}$$

If χ and χ' are the initial and final values of χ, the angle between the two sets of scratches, then the co-ordinates $(x_1, y_1, 0)$ after compression of a point in the upper face of the specimen are related to the co-ordinates $(x_0\ y_0, 0)$ of the same particle before compression by the equations

$$\left.\begin{aligned} x_1 &= \alpha x_0 + \left(\beta \frac{\cos \chi'}{\sin \chi} - \alpha \cot \chi\right) y_0 \\ y_1 &= \beta \frac{\sin \chi'}{\sin \chi} y_0 \end{aligned}\right\} \tag{4}$$

If the particle whose displaced position is being discussed does not lie in the upper surface of the specimen, the transformation formulæ equivalent to (4) are

$$\left.\begin{aligned} x_1 &= \alpha x_0 + l y_0 + \mu z_0 \\ y_1 &= m y_0 + \nu z_0 \\ z_1 &= \gamma z_0 \end{aligned}\right\} \tag{5}$$

where

$$\left.\begin{aligned} l &= \beta \frac{\cos \chi'}{\sin \chi} - \alpha \cot \chi \\ m &= \beta \frac{\sin \chi'}{\sin \chi} \end{aligned}\right\} \tag{6}$$

and μ, ν, γ are to be determined from the measurements of the specimen Of these γ* evidently represents the ratio t_1/t_0 where t_0 and t_1 are the initial and final thicknesses of the specimen These were measured with a micrometer To find μ and ν the co-ordinates of the point 5′ (i e , the central point on the lower face of the specimen) are first found from the measurements If these are $(X_0, Y_0, -t_0)$ before compression and $(X_1, Y_1, -t_1)$ after compression, equations (5) become

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* B L., p 652

$$\left.\begin{aligned} X_1 &= \alpha X_0 + lY_0 - \mu t_0 \\ Y_1 &= mY_0 - \nu t_0 \end{aligned}\right\}$$

and solving these equations

$$\left.\begin{aligned} \mu &= \frac{X_1 - \alpha X_0 - lY_0}{-t_0} \\ \nu &= \frac{Y_1 - mY_0}{-t_0} \end{aligned}\right\} \qquad (7)$$

Hence, all the coefficients in the transformation formulæ (5) can be found from the measurements

Calculation of the Unstretched Cone

To find the unstretched cone we must substitute from (5) in the equation

$$x_0^2 + y_0^2 + z_0^2 = x_1^2 + y_1^2 + z_1^2 \qquad (8)$$

The equation of the cone in the material before distortion is found by eliminating x_1, y_1, z_1, between (5) and (8) It is

$$\begin{aligned} x_0^2(\alpha^2 - 1) + y_0^2(m^2 + l^2 - 1) + z_0^2(\gamma^2 + \mu^2 + \nu^2 - 1) \\ + 2x_0y_0\alpha l + 2x_0z_0\alpha\mu + 2y_0z_0(\mu l + m\nu) = 0 \qquad (9) \end{aligned}$$

The equation of the cone in its distorted position could be found by eliminating x_0, y_0, z_0 from the same two equations Expressing (9) in spherical polar co-ordinates chosen so that θ is the angle which the direction considered makes with the axis of z, and ϕ the angle between its projection on the plane $z = 0$ and the axis of x, equation (9) becomes

$$\begin{aligned} \{(\alpha^2 - 1)\cos^2\phi + (m^2 + l^2 - 1)\sin^2\phi + 2\alpha l\cos\phi\sin\phi\}\tan^2\theta \\ + \{2\alpha\mu\cos\phi + 2(l\mu + m\nu)\sin\phi\}\tan\theta + \gamma^2 + \mu^2 + \nu^2 - 1 = 0 \quad (10) \end{aligned}$$

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* In this work γ is used to denote the ratio of the thickness after any given compression to the thickness before The symbol ε is used to characterize the state of the material at any stage, and represents the ratio of the thickness at that stage to the initial thickness before any compressive stress had been applied Thus, if the material were successively subjected to two compressions and the corresponding values of γ were γ_1 and γ_2, the value of the characteristic ε would be 1 before starting the first test, γ_1 after the first test and before the second, and $\gamma_1 \times \gamma_2$ after the second test

Taking a series of value of ϕ, the corresponding pairs of values of θ can be found from (10) and the cone can then be plotted in a stereographic diagram

Determination of Crystal Axes

In all cases the orientation of the crystal axes was determined* with reference to the ruled generators before the single crystal bar had been cut up into discs The axes were then determined again by X-ray reflections taken at points on the plane faces of the disc-shaped specimens, and it was found that good agreement was obtained, the differences in orientation being never greater than 2° This agreement showed that the method adopted for cutting up and marking the specimens was sufficiently accurate for our purpose, so that we could rely on knowing the orientation of the crystal axes of all the discs into which the original single crystal bar had been cut

After compression, the orientations of the crystal axes were re-determined, and to do this it was sometimes found necessary to etch away one of the faces in order to remove the layer of aluminium which had been in contact with the steel-compressing plate In these circumstances, if the etching had to be carried to a depth which made the fiducial marks indistinguishable, it was still possible to rule a new mark on the etched face and to determine the orientation of the axes with reference to that The specimen could then be mounted in the holder shown in fig 5, and the angle between the new mark and the original fiducial marks on the unetched face determined by reversing the holder on the microscope stage

A difficulty arose in setting the specimen up in the X ray spectrometer If the specimen was fixed to the plane face of a bar which was parallel to the axis of rotation of the spectrometer, only one reflection could usually be obtained with homogeneous X-rays from a copper or iron anticathode To determine completely the orientation of the axes it is necessary to have two reflections, and in order to satisfy this requirement it was desirable to be able to rotate the specimen about an axis perpendicular to the axis of rotation of the spectrometer For this purpose the holder shown in fig 6 was designed

Two pieces of brass angle A, B (fig 6A), soldered together and to a piece of cylindrical brass rod C, form the frame of the holder, which is mounted on the universal table of the X-ray spectrometer, its lower end fitting in the attachment provided for the long cylindrical specimens for which the spectrometer was designed Four pieces of half-round steel D soldered to this frame, as shown,

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* The method used was that described by Dr A Müller, 'Roy Soc Proc,' A, vol 105, p 500 (1924)

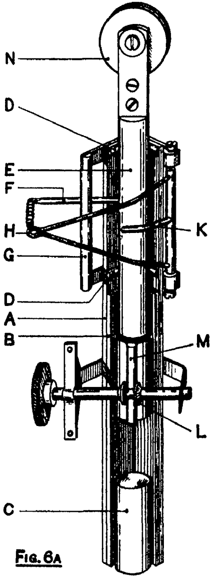

FIG. 6A

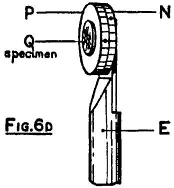

FIG. 6D

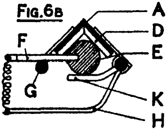

FIG. 6B

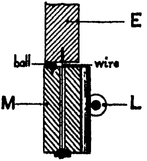

FIG. 6C

Fig 6 —Holder for mounting specimen in X ray spectrometer

form two vees in which the cylindrical slider E rests, touching at four points The slider is prevented from rotating about its axis by a steel rod F fixed to it, which bears against another steel rod G fixed to the frame, making the fifth point of contact The rod G is adjusted to be parallel to the slider E when the latter is resting on the vees This can be done with all the accuracy necessary to ensure that there is no appreciable rotation of the slider as it is moved longitudinally

The slider is kept firmly in position against all the five points of contact with the frame by the system of springing shown in figs 6A and 6B A spring is attached to the end of the rod F and to a pivoted triangular framework H To the latter is fastened a rod K, which presses on the back of the slider E

The slider is moved axially by the mechanism shown in fig 6A and 6C, which was copied from an instrument made by the Cambridge Instrument Company A small grooved pulley L is pressed against a piece of steel rod which is soldered to a cylindrical piece of brass M When rotated by the knurled wheel shown it acts in the same way as a rack and pinion, but much more smoothly The attachment to the slider is by means of the ball and wire shown in fig 6C, these are arranged so as to produce no constraint except the desired axial one

To the upper end of the slider E is attached a circular brass disc N, 2 5 cm in diameter, shown in figs 6A and 6D A second similar disc P is held in frictional contact with N, and is capable of being rotated coaxially with it The specimen Q is stuck on to the face of the disc P with shellac The edges of the discs are graduated, N with 40 and P with 36 divisions This forms a continuous vernier, and is a convenient arrangement when the available diameter is small

In use the specimen is mounted as described, and any one of the lines ruled on its surface is focussed in the microscope of the spectrometer The disc P is then rotated until this line remains on the cross wire, when the slider E is moved axially By adjusting the universal table of the spectrometer, this line is then made to coincide with the axis of rotation of the table Finally, the specimen is rotated in azimuth until its plane contains the direction of the incident beam of X-rays, as ascertained by sighting through the two apertures which define the beam. By reading the azimuth graduations on the universal table, and the vernier on the discs N and P, the orientation of the specimen is completely determined, and that of the crystal planes can then be ascertained by noting the readings of both these scales when the appropriate X-ray reflections are obtained

It will be seen that this holder serves two purposes First, the up and down movement of the slider enables the specimen to be set so that the line selected (and not merely a point on it) is accurately on the axis of rotation of the spectrometer table Secondly, the graduated discs enable the specimen to be rotated in its own plane through any desired angle The reading of the vernier is to 1°, but $\frac{1}{2}$° can be estimated with ease

Choice of Specimens

The orientation of the crystal axes with reference to the flat faces of the specimen can be represented on a stereographic diagram which is exactly equivalent to the figure used in the case of tensile tests, except that the centre of the projection now represents the normal to the disc instead of the axis of the tensile test piece If the axes are now rotated till a cubic (100) axis is in the centre of the projection,* the position on this diagram of the point representing the normal to the plane of the flat faces of the specimen is sufficient to define completely the relationship between this normal and the crystal axes By rotating the appropriate cubic axis into the centre it is always possible to make this point come into a given spherical triangle the corners of which are a (100), a (110) and a (111) axis †

For the experiments to be described three single crystal bars were chosen They were numbered 59, 61 and 69, and their representative points which are shown in fig 7, are well separated in the triangle The disc-shaped specimens

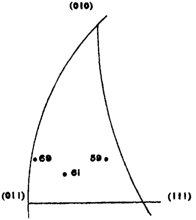

Fig 7 —Stereographic diagram showing orientations of three specimens

out from No 59 were numbered 59 1, 59 2, 59 3 , those from 61 were fig 7, 61 1, 61 2, , etc Many were spoiled in the preliminary experiments necessary to find out how to carry out the compression so as to get uniform distortion, and even when uniform distortion had apparently been obtained it was in some cases necessary to develop methods for ensuring that the friction between the aluminium and the steel plates was the minimum possible before we could be sure of being able to repeat measurements of compressive pressure with different specimens cut from the same bar

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* This projection is shown in P E, p. 31, fig 1

† See P E, figs. 3, 4, 5 and 9

Experiments with No 59

The first experiments were carried out with discs cut from No 59 It was found that they became roughly elliptical when compressed The distortion was uniform over the central part of the disc, but there were two regions, one at each end of the major axis, where the distortion was different from that in the middle Ruled scratches which crossed into these regions were bent at their boundaries The general appearance of the specimens after compression is that shown in fig 8, where the two regions of extraordinary distortion are shown as AB and A_1B_1 In the sketch the region AB is larger than the region A_1B_1, but on the underside the region A_1B_1 would be identical in appearance with the region AB on the upper face, and *vice versâ*, the region of extraordinary distortion being thus symmetrical with respect to the centre of the specimen The boundaries of these regions could be made visible in the compressed specimen by etching with caustic soda

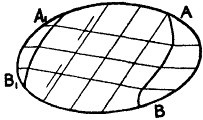

FIG 8 --Appearance of discs cut from No 59 after compression

It will be seen later that the distortion in the main body of the specimen was due to slip on one crystal plane In most parts of the specimen its section by a slip plane consists of a four-sided figure with two straight parallel sides and two curved sides In the neighbourhood of regions AB and A_1B_1 these slip planes cut the specimen in D-shaped figures with one straight side and one curved side It seemed probable, therefore, that the regions of non-uniform distortion could in this case be reduced by reducing the thickness of the specimens It was found that this was true, and it was found also that if the elliptic specimen was turned down into a circular disc, thereby removing the regions AB and A_1B_1, the specimen would distort quite uniformly throughout its volume on further compression The specimen shown in the photograph, fig 2, was cut from No 59, and was first compressed 8 per cent (*i e*, to 92 per cent of its initial thickness) The regions of extraordinary distortion were then removed as described above, the specimen being turned down to the circular disc shown on the first photograph It was then marked,* and finally compressed a further 33 per cent (*i e*, to 62 per cent of its initial thickness), the result being shown in the second photograph It will be seen that the marks remained straight throughout, the boundary being therefore elliptical

These regions of extraordinary distortion occurred only in discs cut from No 59 With Nos 61 and 69 it was found that the distortion was uniform throughout during the whole test

59 6 -The initial dimensions of disc No 59 6 were 14 135 mm diameter and 2 083 mm thick It was compressed by a load of 1 ton in one operation and its final thickness was 1 903 mm The other measurements, when reduced in accordance with formulæ (2) and (3) gave—

$\alpha = 1\cdot00303$ $\quad X_0 = -0\cdot217$ mm

$\beta = 1\cdot0937$ $\quad Y_0 = -0\cdot144$

$\gamma = 0\cdot9134$ $\quad X_1 = -0\cdot212$

$\chi = 90°10'$ $\quad Y_1 = -0\cdot169$

$\chi' = 91°30'$

Hence using (6) and (7) it is found that

$$l = -0\cdot0259, \quad m = 1\cdot0934, \quad \mu = +0\cdot0345, \quad \nu = -0\cdot0326$$

The equation of the unextended cone is

$$(0\cdot00607\cos^2\phi - 0\cdot0516\cos\phi\sin\phi + 0\cdot1960\sin^2\phi)\tan^2\theta$$
$$+ (0\cdot0692\cos\phi - 0\cdot0731\sin\phi)\tan\theta - 0\cdot1634 = 0 \quad (11)$$

This cone is represented by the broken line on the stereographic diagram shown in fig 9 In this diagram the centre O represents the normal to the face of the specimen, while the point X represents the direction of the ruled line on the upper surface of the specimen which is taken as $\phi = 0$

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* The marks on this specimen were made specially deep—see footnote, p 532

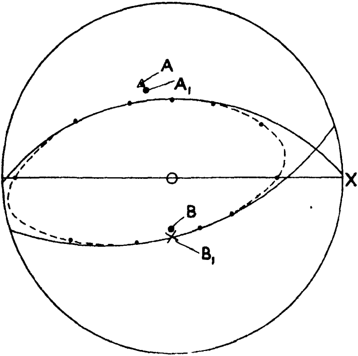

FIG 9 —Stereographic projection of unstretched cone for disc No 59 6 before compression

It will be seen that the projection of the unstretched cone is a closed curve, but on laying the tracing paper on which it was drawn over a stereographic net it was found that this cone very nearly coincided with two planes These two planes are shown as full lines in fig 9 The figure is very similar to those found for the distortion in a tensile test * It seems likely, therefore, that the distortion is due to slipping parallel to one crystal plane It will be seen later† that the experiment can be carried out under conditions which give rise to an unextended cone which is accurately two planes For this reason in the further analysis of specimen No 59 6 the nearest two planes, namely those shown in fig 9, have been regarded as equivalent to the unextended cone

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* P E, fig 2, p 36, and B L, fig 7, p 654

† See p. 549 below

In the case of the tensile test pieces used in our previous experiments, the stress must be uniformly distributed over the cross-section of the bar, and in these circumstances it was shown that, in general, slipping occurs only in one octahedral (111) plane and parallel to a (110) direction It was shown further that, of the 12 possible crystallographically similar shears of this type, the one which occurs is that for which the component of shear stress in the direction of slip is the greatest In the case of the compression tests here described, the stress cannot be quite uniform at all points, because the friction between the steel plates and the specimens cannot be reduced to zero, but on the other hand it was found that the measures taken to reduce friction did have the effect of making the distortion uniform throughout the specimen. It appears likely, therefore that the friction is not great enough to cause any considerable variation of stress in different parts of the specimen Assuming this to be the case, it is possible, if the orientation of the crystal axes is known, to calculate the components of shear stress corresponding with each of the twelve kinds of shear which were shown to be possible in the case of bars in tension Choosing that one of the twelve for which the component of shear stress in the direction of shear is greatest, we can predict the orientations of the plane and direction of shear The method used for making this choice was identical with that previously described in the case of tensile test pieces *

If there is no friction between the specimen and the steel plates, the shear stress corresponding with any particular type of shear is equal in magnitude but opposite in sign to the shear stress which would exist in a tensile test piece whose cross-section coincided with a flat face of the compression specimen, provided the tensile load in the one case was equal to the compressive load in the other For the purpose of predicting the slip plane and direction of slip, therefore, we may identify the normal to the surface of the compression specimen with the axis of the tensile test piece and apply directly the method described previously *

Applying this method to measurements of the orientation of the crystal axes made by Miss Elam, it was found that the co-ordinates of the pole of the predicted slip plane were ($\theta = 59°$, $\phi = 108°$), while those of the direction of slip were ($\theta = 33°$, $\phi = 269°$) These points are marked in fig 9 as A and B

The pole of one member of the pair of planes determined by the distortion measurements is shown at A_1 in fig 9 Its co-ordinates are $\theta = 55°$, $\phi = 107°$ The direction of slip is the point on the slip plane which lies at 90° from the intersection of the two planes which constitute the unextended cone The

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* P E, p. 30.

projection of this direction is shown at B_1 in fig 9 Its co-ordinates are ($\theta = 37°$, $\phi = 270°$) It will be seen that the predicted positions of A and B are close to their observed positions A_1 and B_1

59·7 —Specimen No 59·7 was first compressed by a pressure of 1·5 tons in one operation, so that its thickness changed from 1·806 mm to 1·472 mm It was then measured and the orientation of its crystal axes determined by X-rays

The measurements gave —

$$\left.\begin{array}{ll}\alpha = 1{\cdot}0153 & X_0 = -0{\cdot}254 \text{ mm} \\ \beta = 1{\cdot}1976 & Y_0 = -0{\cdot}236 \\ \gamma = 0{\cdot}817 & X_1 = -0{\cdot}379 \\ \chi = 89° 45' & Y_1 = -0{\cdot}173 \\ \chi' = 94° 10' & \end{array}\right\} \quad (12)$$

and the equation to the unextended cone in its second or compressed position is

$$(0{\cdot}0300 \cos^2 \phi - 0{\cdot}1480 \cos \phi \sin \phi + 0{\cdot}292 \sin^2 \phi) \tan^2 \theta + (0{\cdot}1766 \cos \phi - 0{\cdot}0901 \sin \phi) \tan \theta - 0{\cdot}511 = 0 \quad (13)$$

The calculated points of this cone are shown in the stereographic diagram (fig 10) as crosses, and the cone is marked in as a broken line As in the case of 59·6 the unextended cone nearly, but not quite, coincides with two planes which are shown as full lines passing nearly through the crosses Neglecting the difference between the actual unextended cone and these two planes, the pole of the slip plane and the direction of slip are shown in fig 10 at A_2 and B_2

The predicted positions of these points derived from X-ray measurements by the methods described above are shown at A and B It will be seen that, except for the divergence of the unextended cone from two planes the agreement is good

While these tests were being made, it was discovered that if the compression was carried out in two or three stages, the specimen being removed from the compression machine and re-greased after each operation, the diminution in thickness was greater than when the whole load was applied at once By successively diminishing the increase in load at each stage, it was found that a limit was reached beyond which a further diminution of the increase in load corresponding with one stage in the operations produced no further increase in the amount of the compression for a given final compressive load It was found, for instance, that with discs 14·3 mm diameter, the curves connecting thickness of the specimen with compressive load were practically identical when the loads were increased by 0·05 and 0·1 tons at each stage, but that if

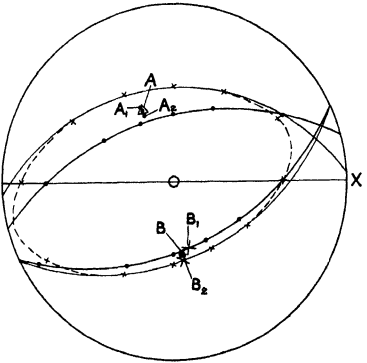

Fig 10.—Unstretched cones for 59·7 in material compressed to $\varepsilon = 0{\cdot}817$

× calculated points for cone corresponding with compression from $\varepsilon = 1{\cdot}0$ to $\varepsilon = 0{\cdot}817$

• calculated points for cone corresponding with compression from $\varepsilon = 0{\cdot}817$ to $\varepsilon = 0{\cdot}817 \times 0{\cdot}8376 = 0{\cdot}684$

the increase was 0·2 tons at each stage there was a measurable increase in the resistance of the specimen to compression It seemed probable, therefore, that by the time the change in load had been reduced to 0·1 tons per stage, the friction had been reduced as much as it was possible to reduce it by this method A reduction in friction increases the uniformity of the stress distribution in the specimen, and if the deviation of the unextended cone from two planes is due in any way to variations in stress in different parts of the specimen, one might expect the unextended cone to approximate more nearly to two planes when the compression is carried out in small stages.

To test this, specimen No. 59·7 was again compressed from 1·423 mm. to 1·192 mm. thick in five stages. Before starting the second test, the specimen which had become elliptical during the first compression was cut down to a circular disc of diameter 12·34 mm., and re-marked with scratches ruled parallel to the original ones. The elements from which the first position of the unextended cone for the second test (*i.e.*, the position in the material when $\epsilon = 0{\cdot}817$)* were calculated are

$$\left.\begin{array}{ll} \alpha = 1{\cdot}0224 & X_0 = -0{\cdot}363 \text{ mm.} \\ \beta = 1{\cdot}1705 & Y_0 = +0{\cdot}031 \\ \gamma = 0{\cdot}8376 & X_1 = -0{\cdot}412 \\ \chi = 94^\circ\ 30' & Y_1 = +0{\cdot}005 \\ \chi' = 100^\circ\ 10' & \end{array}\right\} \qquad (14)$$

The equation to the cone is

$$\begin{aligned} &(0{\cdot}0453 \cos^2\phi - 0{\cdot}259 \cos\phi \sin\phi + 0{\cdot}355 \sin^2\phi) \tan^2\theta \\ &\qquad + (0{\cdot}053 \cos\phi + 0{\cdot}044 \sin\phi) \tan\theta - 0{\cdot}2972 = 0, \end{aligned} \qquad (15)$$

and its stereographic projection is shown in fig. 10, where the points calculated from (15) are represented by round dots. It will be seen that in this case the cone is, to the limit of accuracy of our measurements, actually two planes. With a stereographic net 20 cm. diameter it was not possible to detect any difference between the cone and two planes. In the light of the results obtained with tensile test pieces, it appears, therefore, that the distortion is in this case a simple shear parallel to one plane. Slip on any other plane could have been detected even if it had given rise to only 1 or 2 per cent. of the whole distortion.

The normal to the plane of slip in the second compression is shown at A_1 and the direction of slip at B_1 in fig. 10. It will be noticed that the distortion measurements determine two planes, one of which is the slip plane. In each case one of the planes has nearly coincided with the position of the slip plane predicted from knowledge of the orientation of the crystal axes, and that has been taken as the slip plane. Fig. 10, however, enables us to choose between the two planes without making use of knowledge derived from X-rays. One member of the pair of planes determined for the first compression nearly coincides with one of those derived from the second compression. This plane has remained unstretched and undistorted in both experiments. It is, therefore, the slip plane It will be noticed that this method of choosing between two possible slip planes leads to the same result as the other method involving the use of X-rays

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* See note p. 538.

Second Position of the Unextended Cone for the Second Compression Test of 59·7 —The equation to this cone can be derived from the data (14) Its equation is

$$(0·0433 \cos^2\phi - 0·210 \cos\phi \sin\phi + 0·241 \sin^2\phi) \tan^2\theta + (0·0576 \cos\phi + 0·0456 \sin\phi) \tan\theta - 0·426 = 0, \quad (16)$$

and its stereographic projection is shown in fig 11 which corresponds with material compressed till its thickness is $\varepsilon = 0·817 \times 0·9376 = 0·684$* of its

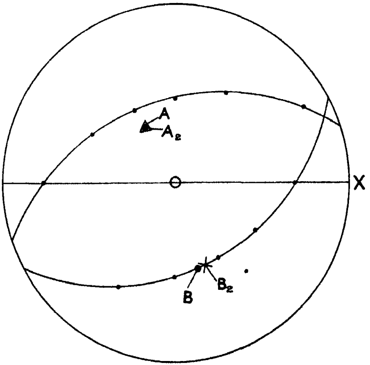

Fig 11 —Second position of unstretched cone for 59·7 during compression from $\varepsilon = 0·817$ to $\varepsilon = 0·684$

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* See note p 538.

original thickness As might be expected, the calculated points lie very accurately on two planes The co-ordinates of the normal to one of these planes are ($\theta = 39°$, $\phi = 118\ 5°$) and the co-ordinates of the corresponding direction of slip are ($\theta = 52°$, $\phi = 286°$) These directions are represented in fig 11 by the points A_2 and B_2

The corresponding directions predicted from X ray measurements were — Normal to slip plane ($\theta = 39°$, $\phi = 118\ 5°$), direction of slip ($\theta = 52°$, $\phi = 290°$) These are marked as A and B in the projection It will be seen that the agreement is very good

We desire to express our thanks to Miss C F Elam, who gave us the single crystal bars used in this work, and carried out all the X-ray measurements Without her help the work could not have been done We wish also to acknowledge the assistance of Dr A Hutchinson, F R S, who allowed us to use measuring apparatus in his laboratory, and of Messrs Armstrong Siddeley Motors, who kindly ground the hardened discs used in compressing the specimens

Most of the work was carried out in the Cavendish Laboratory, through the kindness of Sir Ernest Rutherford We are also indebted to Prof C E Inglis for allowing us to use the compression testing machines in the Cambridge Engineering Laboratory

Summary

The result of the work here described may be summed up in the statement that, so far as these experiments go, the distortion of a crystal of aluminium under compression is of the same nature as the distortion which occurs when a uniform single-crystal bar is stretched The distortion is due to slipping parallel to a certain crystal plane and in a certain crystallographic direction, and the choice of which of twelve possible crystallographically similar types of slipping actually occurs depends only on the components of shear stress in the material and not at all on whether the stress normal to the slip plane is a pressure or a tension

Isotherms of Hydrogen, of Nitrogen, and of Hydrogen-Nitrogen Mixtures, at 0° and 20° C, up to a Pressure of 200 Atmospheres

By T T H VERSCHOYLE

(Communicated by Dr F A Freeth, F R S —Received March 6 1926)

§ 1 *Introduction*

From the work carried out and the statements made by several authors (*cf* § 10 of this paper) it seems that, in the case of mixtures of the "permanent" gases the *pv* values at normal temperatures should be linear functions of the composition Since this assumption has been based principally upon the experimentally determined isotherms of air in relation to those of oxygen and nitrogen, it would appear desirable to investigate the mixtures of some other pair of gases and for this purpose hydrogen and nitrogen have been selected In the case of hydrogen, the determinations of isotherms which have been made at 0° and 20° C by various authors are reasonably concordant, and probably represent a high degree of accuracy, but the agreement between the experimental isotherms of nitrogen leaves much to be desired Moreover, no work whatsoever appears to have been published on the isotherms of hydrogen nitrogen mixtures

Before proceeding to the description of the apparatus used in this research, a brief account and criticism of previous work will be given This account deals only with modern determinations and does not consider Amagat s results, which were obtained at a time when the resources of modern technique were not available, and were published in such a form that a criticism of his results is scarcely possible.

§ 2 *Previous Determinations of the Isotherms of Hydrogen at* 0° *and* 20° *C*

The isotherm of hydrogen at 0° C has been determined at Leiden by Kamerlingh Onnes and Braak,* and at the Physikalisch Technische Reichanstalt, Berlin, by Holborn † The Leiden measurements, which extend only to 50 atmospheres, are open to some objection As is the general practice in the determination of isotherms at Leiden, the volumes occupied by one and the same quantity of gas at different pressures are measured, so that the probable errors in the values of *pv* increase with increasing pressure. provided, however, that a sufficient quantity of gas be used, the errors can, of course, be kept within any limits desired. Two types of piezometer are employed, the "simple" (or undivided) and the "divided" model. The simple type, which is generally used in determinations at temperatures above the freezing-point of mercury, is represented in fig. 1. It consists essentially of a cylindrical stem S, the bore of which is carefully calibrated over the whole length, and of a large reservoir R of known volume. The piezometer is secured in a compression vessel by means of a collar, and the determination of an isotherm consists, in principle, in compressing a known volume of gas over mercury into successive known volumes of the stem at a constant temperature.

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* 'Phys Lab,' Leiden Commn No 100B

† 'Ann d Physik,' vol. 63, p 674 (1920)

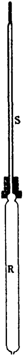

Fig. 1 (left) — Simple Piezometer.

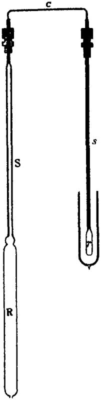

Fig. 2 (right) — Divided Piezometer.

For temperatures below the freezing-point of mercury, the divided type illustrated in fig. 2 is used. The stem S is connected through suitable couplings and a flexible metal capillary *c* to the small reservoir *r* (of known volume), which can be exposed to a low temperature. The normal volume of gas in the small reservoir can be derived from a knowledge of the total volume of the gas and of the volume in the rest of the apparatus (maintained at normal temperature). In the case of the isotherm at 0° C., a divided piezometer was used, only the gas in the small reservoir (volume 10, cm.³) being at a temperature of 0° C. The gas in the stem of the piezometer (maximum volume, 12 cm.³) was at normal temperature (20° C.), and the normal volume of the gas at 0° C. determined by difference. The accuracy of the results therefore depends on an accurate knowledge both of the normal isotherm (at 20° C.) and of the volumes of the different portions of the piezometer. Now these portions (piezometer stem small reservoir, and connecting steel capillary) were all directly calibrated by mercury, and it has recently been pointed out by Penning[*] that small spaces of unknown volume may exist in the soldered joints between the couplings and the glass capillaries to which they are affixed All the measurements at Leiden with divided piezometers are liable to objection on this ground (except where some suitable check has been afforded), more especially when the density of the gas in the small reservoir is not much larger than that in the stem, as is the case here Moreover only four points were measured, so that it is difficult to form any idea of the probable errors involved The determinations of pressure and temperature were, as is always the case at Leiden, unexceptionable

The method in use at Berlin for the determination of isotherms[†] differs from the Leiden method in that the volume into which the gas is compressed is constant, the quantities of gas used thus increasing with the pressure The sensitivity of the measurements therefore does not decrease with increasing pressure, and, as comparatively large quantities of gas were used (the confining volume was about 110 cm ^{3}), the volume observations, *cet par*, should be extremely accurate Normal volumes are measured only after the observations at high pressures, in a series of flasks contained in a large water bath Pressures are measured on a pressure balance fitted with a mechanism for imparting an oscillatory motion to the piston The balance was calibrated with the help of an open manometer so that the pressure determinations should also be very satisfactory It appears from the results that the errors of observation seldom exceeded 1 in 4,000, and, up to 100 atmospheres (the highest pressure reached), the isotherm at 0° C is undoubtedly very accurate

The isotherm at 20° C has been repeatedly measured at Leiden The determination by Schalkwijk,[‡] using an undivided piezometer, stands in a class by itself, for it was effected with extraordinary care and precision, unfortunately it reaches only to 60 atmospheres Kamerlingh Onnes, Crommelin, and Smid[§] have extended the isotherm at 20° C to 100 atmospheres, and the *pv*-value found for the highest pressure differs by 1 in 700 from that derived from an extrapolation of Schalkwijk's equation The lowest pressure measured was 65 atmospheres, and the *pv* value found differed only by 1 in 3,000 from Schalkwijk's value Since, however, the differences all lie in the same direction, it would seem that some small systematic error was involved, and Schalkwijk's equation is probably to be preferred

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[*] 'Phys Lab,' Leiden Commn. No 166

[†] Holborn and Schultze, 'Ann. d Physik,' vol 47, p 1089 (1915)

[‡] 'Phys Lab,' Leiden, Commn No 70

[§] 'Phys Lab,' Leiden, Commn No 146B

At Amsterdam, where the isotherm has been determined by Kohnstamm and Walstra,* the range of pressure covered was much wider, extending to 1,000 atmospheres As at Leiden, a constant quantity of gas was used, but the method of determination was more complicated and not so direct Pressures were measured with a pressure-balance, which, however, had not been calibrated either directly or indirectly against an open manometer, so that the effective cross-section of the differential piston was not known with certainty, the error involved was probably small The volumes of the compressed gas were determined by Amagat's method of electrical contacts in a glass tube, this method is apparently quite satisfactory It was not possible to determine the normal volume directly, and therefore, after a relation between pv and $1/v$ had been derived in arbitrary units, it was reduced to an equation in which the constant term had the same value as found by Schalkwijk The agreement between the pv-values derived from this final equation with those derived from Schalkwijk's equation (extrapolated above 60 atmospheres) is very good up to 120 atmospheres, and the mutual agreement between the several experimental series is also very satisfactory

No direct measurement has been made at Berlin of the isotherm at 20° C, but an equation can be quadratically interpolated between the isotherms at 0°, 50°, and 100° C (Holborn, *loc cit*), and this agrees excellently with Schalkwijk's equation Thus, although the latter was experimentally established only up to a pressure of 60 atmospheres, its validity up to 100 atmospheres may be safely assumed

§ 3 *Previous Determinations of the Isotherms of Nitrogen at 0° and 20° C*

The measurement at Berlin of the isotherm of nitrogen at 0° C by Holborn and Otto† was carried out by the same methods as in the case of hydrogen, so that no further criticism of these methods is necessary The nitrogen used came from a commercial source, and may, therefore, have contained traces of the rare gases, its density, however, was satisfactory

At Leiden, the isotherm at 0° C has been determined by Kamerlingh Onnes and van Urk,‡ using in this case an undivided piezometer, so that no objection can now be raised against the volume measurements The normal volume was measured only before the determination of the isotherm and thus no check upon its accuracy was available but the possibility of an alteration in its value was very slight. The nitrogen was chemically prepared by the reaction between ammonium chloride and sodium nitrite in the presence of potassium dichromate, and it was purified by a passage through aqueous ferrous sulphate and over hot copper. Hence it was probably reasonably pure. The concordance between the Berlin and the Leiden results over the range which the latter cover is satisfactory.

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* 'Proc. Roy Acad, Amsterdam,' vol 17, p 203 (1914)

† 'Z f Physik,' vol 23, p 77 (1924)

‡ 'Phys Lab,' Leiden, Commn No 169D

The determination of the isotherm at 0° C. by Smith and Taylor* at Boston, by an isometric method is of particular interest, both because the pressures involved extended to 160 atmospheres, and on account of the ingenuity of the apparatus used; *unfortunately, the results are apparently affected by a comparatively large systematic error*, as will be seen from subsequent considerations. The design of the apparatus is due to Keyes and, in so far as the measurements of pressure and temperature are concerned, no objection can be raised. As at Leiden, a constant quantity of gas is used in the determination of the isometrics but the volumes occupied by this quantity at the several pressures and temperatures are not determined by a direct method, for they are derived indirectly from a measurement of the volume of the piston used in displacing the confining mercury. An accurate volume determination presupposes, therefore, complete absence from the smallest leak of mercury at all joints and at the gland through which the piston passes, together with a very accurate calibration of the volumes of the piezometer and the piston, especially as the total volume of the confined gas at the highest pressures was only about 2 cm.^{3}

If the method of measuring the volumes be admitted as satisfactory, yet the preparation and purification of the nitrogen used in the determination is open to serious criticism. The gas was prepared by the reaction between ammonium sulphate and potassium nitrite, dried, condensed and "fractionally distilled." No chemical method was applied for removing the nitric oxide which is always formed in this reaction, and, during the fractional distillation, no device appears to have been adopted to ensure the boiling of the liquefied gas, without which, of course, no fractionation occurs. It is by no means easy to make a liquefied gas boil evenly, unless precautions are taken to do so, such as by means of a heating coil. The only criterion given for the purity of the gas is that "the resulting liquid nitrogen was water white and entirely free from solid impurities," which, of course, is no criterion at all. Since the pv values derived from the Boston results are considerably lower than both the Berlin and the Leiden values, it seems highly probable that the nitrogen used contained appreciable quantities of nitric oxide

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* 'J. Am. Chem. Soc.,' vol. 45, p. 2107 (1923).

The isotherm at 20° C has been directly determined only at Leiden, by Kamerlingh Onnes and van Urk (*loc cit*) As in the case of hydrogen, an isotherm can be quadratically interpolated between the Berlin isotherms at 0°, 50°, and 100° C (Holborn and Otto, *loc cit*), and this agrees very well with the Leiden isotherm An interpolation between the Boston isotherms at 0°, 50°, and 100° C gives an equation which leads to comparatively low values of *pv*

§ 4 *Experimental Apparatus*

The apparatus employed in the present research is largely based on that used at Leiden for the determination of isotherms, so that a detailed description is unnecessary The general principle consists, as at Leiden, in the compression of a known constant quantity of gas into measured volumes, the smallest volume was never less than 4 cm^3 Whereas at Leiden, however, the normal volume is measured in the piezometer itself (for which purpose the piezometer has to be removed from the compression vessel), the piezometer is here permanently mounted, and the normal volume measured in a volumenometer, from which the gas is transferred to the piezometer The whole apparatus may conveniently be considered under the following headings —

(*a*) Mixing apparatus
(*b*) Volumenometer
(*c*) Piezometer
(*d*) Pressure balance
(*e*) Thermostat

(*a*) ***Mixing Apparatus***—This is a simple arrangement for making up mixtures of known composition The pressure and temperature of each gas are measured at constant volume in a water-jacketed bulb of about 1 l capacity, and the gases are then driven successively into a second bulb, of 2½ l capacity

(*b*) ***Volumenometer***—In the volumenometer the normal volume of the simple gas or mixture is measured The apparatus is a copy, somewhat modified, of that in use at Leiden,* and is represented in fig 3 It consists essentially of a series of three bulbs B, each of about ¼ l capacity, connected by necks on which marks are etched, the volumes between the marks are known from previous calibrations, as are also the volume between taps 1 and 2 and the top mark, and the volume between taps 2 and 3 The bulb-tube is connected

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[*] *Cf* 'Phys Lab,' Leiden, Commn Nos 117 and 127*c*.

through an air-trap to a manometer M, and to a common mercury reservoir R. Both the bulb tube and the manometer are surrounded by water jackets,

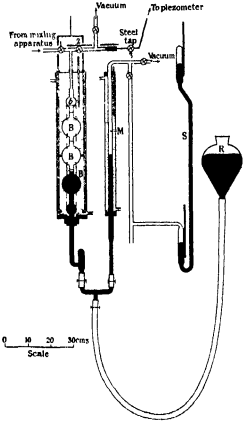

Fig. 3.—Volumenometer.

through which a stream of water flows from a thermostat. The top of the manometer can be connected either to a syphon barometer S or to a vacuum-pump, as may be desired.

The positions of the mercury menisci in the volumenometer are observed with a cathetometer, by the Société Genevoise, reading to 0·02 mm. Both volumenometer and cathetometer are mounted on a heavy slate slab, supported on a large concrete table and foundation, and are satisfactorily free from the effects of vibration.

(*c*) *Piezometer* —The piezometer is based on the divided model employed at Leiden but differs from it in several respects In the first place, it should be explained that a divided type was used because the whole apparatus was designed and constructed primarily with a view to use at low temperatures The disadvantages of the divided type mentioned in § 2 are however eliminated by a volumetric calibration with gas instead of a direct calibration with mercury

The use of a divided piezometer is attended with several difficulties The volume of the small reservoir can scarcely be determined with a greater accuracy than 1 mm ^{3} and therefore it should be at least 1 cm ^{3} If this volume is to be filled with a liquefied gas at low temperature the volume of the large reservoir of the piezometer must be about 1 l It is hardly possible to maintain an even temperature over a greater length of stem than 50 cm and if the piezometer is to have a useful pressure range of at least 3 or 4 l the bore of the stem must hence be 4 mm or more Long and wearisome trials of several kinds of glass tubing completely confirmed the experience of previous investigators as to the utter untrustworthiness of glass tubes when exposed to pressures above 60 atmospheres no matter what the thickness of wall Tubing of the desired bore that had withstood test pressures as high as 270 atmospheres on several successive days eventually burst at 90 atmospheres

It was therefore necessary to construct the piezometer entirely of metal for there appeared to be no practicable method of securing a glass tube at *both* ends within a compression cylinder with a view to making observations by Amagat s method of electrical contacts (in the case of an undivided piezometer the glass tube has to be fastened only at *one* end and that is quite feasible) Some new method of measuring the position of the mercury had also to be devised, and it was suggested by Mr L W Codd of this laboratory that this might be effected by measuring the resistance of a fine platinum wire stretched down the centre of the stem after an extensive series of tests this device has been adopted A relation between the resistance of the wire and the volume included between the top of the stem and the surface of the mercury was established by compressing a known volume of hydrogen into the stem at a temperature of 20° C and measuring the resistance at several pressures the volume occupied by the hydrogen in each case being derived from a knowledge of the well established isotherm of that gas up to a pressure of 100 atmospheres It is of course only possible in this way to determine the position of the highest point of the mercury in the stem the height of the meniscus cannot be measured Great accuracy in the volume determinations is hence not to be expected, but, for a long period, the actual results were much worse than was anticipated, discrepancies occurring to the extent of 2 per cent No reason for this could be found but fortunately these large errors suddenly disappeared of themselves and the results of the isotherms show that the mean error of observation is now always less than 1 in 1 000 The resistance volume factor for the wire is not entirely constant but the change over the whole of the series of the present investigation was less than 1 in 500

A section of the steel piezometer and the compression vessel (or pot) into which it is fastened is shown in fig 4 The stem S has a bore of 8 mm

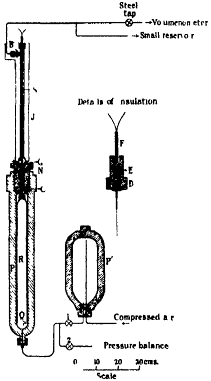

Fig 4 —Piezometer and Compression Vessel Inside (on right) Details of Insulation

and a total length of 70 cm and it is integral with the collar C whereby it is secured in the pot P with the help of the split nut N the bore is ground true and highly polished A flange G which is also part of the stem acts as the base of the water jacket J The lower end of the stem forms a boss on to which the large reservoir R, of about 900 cm ^{3} capacity, is screwed, R is closed by a cap Q, with a small opening in the centre The pot P is connected with a second pot P′, which acts as a reservoir for the mercury When pressure is applied on the air-main, the mercury is forced from P′ into P, and thus up into the piezometer A branch leads from the steel capillary connecting P and P′ to the pressure-balance The general lay-out of the air connections is much the same as at Leiden,* with the exception that the closed hydrogen manometer is here replaced by the pressure-balance

After pressure has been applied with the help of compressed air, tap 1 is closed, thereby cutting off P′ and the air connections, and communication with the pressure-balance is established exclusively by liquids through tap 2 The final adjustment of the pressure is carried out by the regulation of the weights on the balance and with the help of the oil pump connected to it

The upper end of the fine platinum wire (about 0 03 mm in diameter) in the stem is welded to a short length of thicker wire which, in its turn, is brazed on to a piece of brass wire The latter is screwed into the lower end of a steel cone F, as shown in fig 4 and this is insulated by a conical ivory ring E from the steel collar D, which is secured by a nut to the screwed top of the stem This method of insulation was adopted by Kohnstamm and Walstra,† and has proved very satisfactory The lower end of the stem wire is welded to one end of a small spiral of thicker platinum wire, the other end of which is secured by a piece of ebonite wedged across the bottom of the stem, in this way the wire is kept as taut as is consistent with safety, and is ordinarily insulated from the stem, electrical contact being made only when the confining mercury is compressed into the latter Double leads from the upper end of the cone F and from the outside of the stem form the electrical connections between the stem wire and the differential galvanometer, resistance-box, and commutator used in measuring the resistance by Kohlrausch's method of overlapping shunts ‡ The stem wire has a resistance of about 1 ohm/cm, and 1 cm on the galvanometer scale corresponds to about 0 005 ohms

The screwed boss B, affixed near the top of the stem, allows of the attachment of a steel capillary (with a bore of 0 5 mm), this divides near the piezometer, one arm leading through a steel tap to the volumenometer, and the other arm to the small reservoir The latter is a brass cylinder of about 1 cm ^{3} capacity, to which the steel capillary is attached by means of a nut and collar It is required for work at low temperatures, and, in the present research, may be regarded more or less as dead space

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* *Cf* 'Phys Lab,' Leiden, Commn No 97A, Plate I

† 'Proc Roy Acad, Amsterdam,' vol 16, p 822 (1914)

‡ Kohlrausch, 'Lehrbuch der Praktischen Physik,' 13th edn., p 427

(*d*) *Pressure-balance* —The pressure-balance was supplied by Schaffer and Budenberg, and the effective cross-section of the differential piston was determined by the Physisch Technische Reichsanstalt, Berlin Between 40 and 240 atmospheres, the difference between this cross-section and the area given by the makers was found to be less than 1 in 2,000—a very satisfactory result As originally supplied, the balance was worked by hand, but an oscillating mechanism, similar to that described by Holborn,* was constructed and fitted to the balance in this laboratory The change from oil to mercury in the transmission from the pressure balance to the piezometer is made in a short vertical length of $\frac{1}{8}$-inch hydraulic steel tubing, into which two insulated electrical contacts are fitted, the mercury meniscus is always kept between these contacts

(*e*) *Thermostat* The thermostat, which delivers a stream of water to the several water-jackets and thence to waste, is a copy of the one described by Schalkwijk (*loc cit*) In the determination of the isotherms at 20° C it was not found possible to maintain the stem of the piezometer exactly at that temperature, owing to the very large variations in the room temperature—the laboratory is really most unsuitable for such measurements so that there was little object in effecting any exact regulation of the thermostat

The isotherms at 0° C were determined by packing the stem of the piezometer in shavings of ice made from distilled water The volume of gas at 0° C was always considerably greater than that at room temperature, so that the objections raised in § 2 against the Leiden determination of the hydrogen isotherm at 0° C apply in much less degree

§ 5 *Preparation of Gases*

Hydrogen was taken from a commercial cylinder of the gas, passed over hot copper and through silica gel maintained at the temperature of liquid air, and stored in a glass gas-holder over mercury Traces of nitrogen may have been left in the hydrogen, but it will be seen later that the presence of even a few per cent of nitrogen hardly affects the course of the isotherm

Nitrogen was prepared by the action of sodium nitrite on ammonium sulphate in the presence of potassium dichromate The gas was passed through a solution of chromic acid in strong sulphuric acid and over red-hot copper, dried, liquefied, and allowed to evaporate into a small steel cylinder Its purity was tested by a vapour pressure determination. At $-195.73°$ C., with only a drop of liquid in the experimental bulb, the vapour pressure was found to be 76.39 cm.; after condensation of an additional ½ l. of gas, the pressure was 76.46 cm. but the temperature was then 0.01° higher. According to the formula given by Cath,* the vapour pressure at $-195.73°$ C. should be 76.52 cm., whilst the difference in pressure corresponding to a difference of 0.01° is 0.08 cm. The purity of the gas thus left nothing to be desired.

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* 'Z d. Ver deut Ing,' vol. 67, part 8 (1923)

Apart from the individual gases, three mixtures, containing respectively 75 per cent., 50 per cent., and 25 per cent. of hydrogen, were investigated.

§ 6. *Units and Empirical Equations.*

Before reproducing the results, it is necessary to discuss the units adopted in expressing them. It has been thought best to retain the units introduced by Amagat, for these are in use at Leiden and are particularly convenient for practical purposes. The unit of pressure (p) is the international atmosphere, and the unit of volume (v_A) is the normal volume, or the volume occupied by the quantity of gas taken at 0° C. under a pressure of one atmosphere. These units are also in use at Amsterdam.

At Berlin the unit of pressure is the pressure exerted by a column of mercury 1 m. in length under standard conditions, and the normal volume is measured at that pressure. The Boston unit of pressure is the atmosphere, and the unit of volume is the specific volume. Neither of these two systems is more rational than Amagat's system, and they do not appear to be so convenient.

The expression of the isotherms in the form of equations also requires consideration. The Leiden isotherms are based on the empirical equation of state established by Kamerlingh Onnes,† and accordingly take the form of a development of the product pv_A in terms of powers of $1/v_A$ $(= d_A)$, *i.e.*,

$$pv_A = A_A + B_A d_A + C_A d_A^2 + \ldots,$$

where A_A, B_A, C_A are constants (higher terms than d_A^2 need not be considered here). For practical purposes this is not a very convenient form, and the Berlin mode of expression will therefore be adopted, pv_A being developed in powers of p, *i.e.*,

$$pv_A = A_p + B_p p + C_p p^2.$$

The subscript p is used to distinguish the constants from the constants A_B, B_B, C_B, appearing in the Berlin equations, and referred to the Berlin units.

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* 'Phys. Lab.,' Leiden, Comm. No. 152D.

† 'Phys. Lab.,' Leiden, Comm. No. 71.

Isotherms determined at Boston are expressed in the form of an equation of state developed theoretically by Keyes This equation involves the assumption that the pressure varies linearly with the temperature at constant volume—an assumption which is common to many proposed equations of state, but is only valid over a limited range * Moreover, the equation is of an unsuitable form for purposes of computation

§ 7 *Experimental Data*

The results obtained in the measurement of the isotherms at 0° and 20° C of hydrogen, nitrogen, and the three mixtures, are reproduced in Tables I–X Both the observed and the calculated values of pv_A are shown for each value of the pressure, whilst the last column contains the difference between the two The calculated values are the values given by the equations, which were derived from the observed values by the method of least mean squares, and are reproduced later on Below each table is given the computed mean error of observation

Table I —Isotherms of H_2 at 0° C

Point	p	pv_A (obs)	pv_A (calc)	O − C
*XIV 1	46 11	1 0280	1 0287	−0 0007
2	53 71	1 0339	1 0347	−0 0008
3	79 79	1 0498	1 0505	−0 0007
4	103 94	1 0655	1 0664	−0 0009
XVI 1	103 94	1 0658	1 0664	−0 0006
XIV 5	128 11	1 0820	1 0825	−0 0005
XVI 2	128 11	1 0831	1 0825	+0 0006
XIV 6	147 45	1 0959	1 0954	+0 0005
XVI 3	147 45	1 0974	1 0954	+0 0020
XIV 7	166 79	1 1101	1 1085	+0 0016
XVI 4	166 79	1 1081	1 1085	−0 0004
XIV 8	186 13	1 1207	1 1218	−0 0011
XVI 5	186 13	1 1212	1 1218	−0 0006
6	195 80	1 1282	1 1284	0 0002
7	205 48	1 1345	1 1351	−0 0006

* Series XIV and XVI were determined with the same normal volume, but on different occasions

Mean error of observation = ± 0 00094

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* *Cf* Penning, *loc cit*, and Kamerlingh Onnes and Keesom, 'Phys Lab.,' Leiden, Commn Suppl No 23, § 42

Table II.—Isotherm of 75 per cent H_2 – 25 per cent N_2 at 0° C

Point	p	pv_A (obs.)	pv_A (calc.)	O – C
II 1	46 07	1 0239	1 0247	0 0008
2	55 68	1 0316	1 0302	+0 0014
3	79 76	1 0443	1 0445	0 0002
4	103 93	1 0 94	1 0594	+0 0000
5	128 09	1 0755	1 0750	+0 0005
6	147 43	1 0884	1 0878	+0 0006
7	166 77	1 1010	1 1011	0 0001
8	186 12	1 1144	1 1146	0 0002
9	195 9	1 1213	1 1217	0 0004
10	205 47	1 1 82	1 1287	0 0005

Mean error of observation ± 0 00064

Table III.—Isotherm of 50 per cent H_2 – 50 per cent N_2 at 0° C

Point	p	pv_A (obs.)	pv_A (calc.)	O – C
IV 1	46 06	1 01 7	1 0162	0 0007
2	55 68	1 0203	1 0204	0 0001
3	79 76	1 0313	1 0315	0 0002
4	103 92	1 437	1 0449	0 0002
5	128 09	1 786	1 0578	+0 0008
6	147 43	1 0703	1 0698	+0 0005
7	166 76	1 0832	1 0828	+0 0004
8	186 11	1 0964	1 0965	0 0001
9	195 79	1 1031	1 1037	0 0006
10	205 46	1 1108	1 1111	0 0003

Mean error of observation = ± 0 00048

Table IV.—Isotherm of 25 per cent H_2 – 75 per cent N_2 at 0° C

Point	p	pv_A (obs.)	pv_A (calc.)	O – C
VI 1	46 06	1 0025	1 0036	0 0011
2	55 67	1 0053	1 0054	0 0001
3	79 76	1 0111	1 0116	0 0005
4	103 92	1 0201	1 0201	±0 0000
5	128 09	1 0314	1 0309	+0 0005
6	147 42	1 0417	1 0413	0 0004
7	166 77	1 0530	1 0531	0 0001
8	186 12	1 0672	1 0664	+0 0008
9	195 79	1 0732	1 0737	0 0005
10	205 46	1 0806	1 0813	0 0007

Mean error of observation ± 0 00060

Table V —Isotherm of N_2 at 0° C

Point	p	pv_A (obs)	pv_A (calc)	O – C
*IV 1	24 74	0 9896	0 9902	0 0006
2	26 65	0 9896	0 9897	–0 0001
3	36 23	0 9873	0 9869	+0 0004
4	45 84	0 9844	0 9848	0 0003
VI 1	46 08	0 9851	0 9847	+0 0004
IV	55 48	0 9827	0 9833	0 0006
VI 2	55 68	0 9843	0 9832	+0 0011
IV 6	74 78	0 9818	0 9820	0 0002
VI 3	79 76	0 9827	0 9821	+0 0006
IV 7	94 12	0 9829	0 9834	0 0005
VI 4	103 92	0 9854	0 9850	+0 0004
†IV 8	113 49	0 9851	0 9872	0 0021
VI	128 09	0 9929	0 9916	+0 0013
	147 43	1 0008	1 0000	+0 0008
	166 77	1 0106	1 0104	+0 0002
8	186 11	1 0244	1 0236	+0 0008
9	195 79	1 0315	1 0312	+0 0003
1	205 46	1 0382	1 0394	0 0012

* Series IV and VI were determined with different normal volumes

† Point IV (8) has been omitted in deriving the equation and in calculating the mean error for the error of observation appears unaccountably large

Mean error of observation = ± 0 00076

Table VI —Isotherm of H_2 at 20° C

Point	p	pv_A (obs)	pv_A (calc)	O – C
XV 1	46 15	1 1030	1 1027	+0 0003
2	55 74	1 1091	1 1090	+0 0001
3	79 81	1 1252	1 1249	+0 0003
4	103 96	1 1408	1 1409	0 0001
5	128 12	1 1559	1 1570	–0 0011
6	147 46	1 1705	1 1700	+0 0005
7	166 80	1 1834	1 1829	+0 0005
8	186 14	1 1905	1 1900	+0 0005
9	195 81	1 2015	1 2026	0 0011
10	205 48	1 2097	1 2091	+0 0006

Mean error of observation = ± 0 00064

Approximately double the quantity of gas was used for the measurement of this isotherm as for the volumetric determination of the resistance volume factor of the stem wire from the course of the known isotherm between 0 and 100 atmospheres

Table VII —Isotherm of 75 per cent H_2 — 25 per cent N_2 at 20° C

Point	p	pv_A (obs.)	pv_A (calc)	O — C
I 1	36 57	1 0940	1 0940	±0 0000
2	46 12	1 1002	1 0998	+0 0004
3	55 71	1 1057	1 1056	+0 0001
4	79 78	1 1209	1 1205	+0 0004
5	103 94	1 1360	1 1362	−0 0002
6	128 11	1 1534	1 1523	+0 0011
7	147 44	1 1658	1 1657	+0 0001
8	166 78	1 1788	1 1795	−0 0007
9	186 13	1 1930	1 1933	−0 0003
10	195 80	1 2003	1 2005	−0 0002
11	205 45	1 2081	1 2077	+0 0004

Mean error of observation = ± 0 00049

Table VIII —Isotherm of 50 per cent H_2 — 50 per cent N_2 at 20° C

Point.	p	pv_A (obs)	pv_A (calc).	O — C
III 1	36 55	1 0894	1 0888	+0 0006
2	46 10	1 0935	1 0932	+0 0003
3	55 70	1 0981	1 0980	+0 0001
4	79 78	1 1107	1 1105	+0 0002
5	103 94	1 1241	1 1243	−0 0002
6	128 10	1 1393	1 1391	+0 0002
7	147 43	1 1518	1 1518	±0 0000
8	166 78	1 1651	1 1652	−0 0001
9	186 12	1 1790	1 1792	−0 0002
10	195 80	1 1863	1 1866	−0 0003
11	205 47	1 1938	1 1941	−0 0003

Mean error of observation = ± 0 00028.

Table IX —Isotherm of 25 per cent H_2 — 75 per cent. N_2 at 20° C

Point	p	pv_A (obs)	pv_A (calc)	O — C
V 1	36 57	1 0809	1 0801	+0 0008
2	46 11	1 0823	1 0825	−0 0002
3	55 71	1 0857	1 0853	+0 0004
4	79 78	1 0937	1 0938	−0 0001
5	103 94	1 1045	1 1042	+0 0003
6	128 10	1 1171	1 1167	+0 0004
7	147 44	1 1283	1 1281	+0 0002
8	166 78	1 1409	1 1405	+0 0004
9	186 12	1 1540	1 1545	−0 0005
10	195 80	1 1617	1 1619	−0 0002
11	205 47	1 1691	1 1696	−0 0005

Mean error of observation = ± 0 00043

Table X—Isotherm of N_2 at 20° C

Point	p	pv_A (obs)	pv_A (calc)	O − C
*III 1	24 78	1 0681	1 0685	−0 0004
2	26 68	1 0679	1 0682	−0 0003
3	36 26	1 0674	1 0673	+0 0001
4	45 86	1 0667	1 0668	−0 0001
V 1	46 13	1 0675	1 0668	+0 0007
III 5	55 50	1 0668	1 0668	±0 0000
V 2	55 71	1 0675	1 0668	+0 0007
III 6	74 79	1 0685	1 0685	±0 0000
V 3	79·78	1 0699	1 0692	+0 0007
III 7	94 12	1 0716	1 0722	−0 0006
V 4	103 94	1 0754	1 0750	+0 0004
III 8	113 50	1 0770	1 0780	−0 0010
V 5	128 10	1 0849	1 0838	+0 0011
6	147 44	1 0941	1 0934	+0 0007
7	166 78	1 1056	1 1048	+0 0008
8	186 12	1 1183	1 1185	−0 0002
9	195 80	1 1260	1 1262	−0 0002
10	205 47	1 1339	1 1343	−0 0004

* Series III and V were determined with different normal volumes

Mean error of observation = ± 0 00058

§ 8 *Observational Equations*

The values of the constants A_p, B_p, C_p in the equations representing the isotherms are contained in Table XI In the derivation of these equations the value of $(A_p)_0$—i e, A_p at 0° C —is found from the relation

$$1 = (A_p)_0 + (B_p)_0 + (C_p)_0,$$

whilst the value of $(A_p)_{20}$ is given by the expression

$$(A_p)_{20} = (A_p)_0 \times (1 + 20\gamma),$$

where $\gamma = 0\ 0036618$, B_p and C_p are then evaluated by the method of least mean squares

Table XI —Values of A_p B_p and C_p

Gas		A_p	B_p	C_p
H_2	at 0 C	0 99937	$+0\ 6263 \times 10^{-3}$	$0\ 168 \times 10^{-6}$
75 per cent H_2 25 per cent. N_2		0 99948	0 5229	0 516
50 per cent. H_2 50 per cent. N_2		0 99969	0 3067	1 147
25 per cent. H_2 — 75 per cent N_2		1 00001	0 0140	1 993
N_2		1 00049	0 4961	3 334
H_2	at 20 C	1 07257	+0 6505	0 069
75 per cent H_2 25 per cent. N_2		1 07269	0 5658	0 448
50 per cent H_2 50 per cent N_2		1 07291	0 3979	0 933
25 per cent H_2 75 per cent N_2		1 07327	0 1225	1 685
N_2		1 07370	0 2798	2 800

The curves representing the equations and the individual points are plotted in figs 5 and 6

§ 9 *Sources and Magnitudes of Errors*

The errors involved in the determination of pressure and temperature were almost certainly negligible in comparison with the errors accompanying the volume measurements The temperatures were read on thermometers graduated in tenths of a degree (1 cm ≡ 1°) which had been checked against a standard thermometer It is improbable that errors in temperature would exceed 1/20° or 0 02 per cent in the values of pv_A

The pressure balance is well known to be a most reliable and accurate instrument and as already stated the effective cross section of the piston between pressures of 40 and 240 atmospheres does not differ by more than 0 05 per cent from the stated actual cross section Probably the most uncertain measurement in connection with the pressure is that of the difference in level between the mercury in the stem of the piezometer and in the tube where the junction with the oil of the balance is made This may amount to 2 cm or to more than 0 1 per cent at pressures lower than 30 atmospheres At higher pressures with which we are chiefly concerned the error would be of little consequence

The total error involved in the volume measurements is not easy to estimate It may be divided into two parts viz the error of the normal volume (constant throughout each series of measurements) and the error of the stem volume (occupied by the gas under the measured pressure). The normal volume was determined before and after each series, and the accuracy of each determination was such that only the error consequent on any difference between the two values need be considered. The mean value was used in the computation, and the greatest difference between the mean and either individual value was 0·04 per cent.

The error of the stem volume may be due to one or more of three causes: droplets of mercury may cling to the wire or to the walls of the stem, the shape of the meniscus may differ considerably from the average shape, or the resistance of the wire may alter. It is scarcely possible to separate the effects of the first two causes, but the fact that the mean error of observation for a series was generally about 0·06 per cent. shows that they cannot have amounted to very much. The meniscus might vary ½ mm. in height, which would lead to an error of 1 in 300 on the smallest volume measured, but the results appear to show that the variation cannot have been nearly so large.

Determinations of the resistance-volume factor of the stem wire at the beginning and at the end of this investigation indicated that this factor had changed by 1 in 500. It is reasonable to suppose that the change was gradual, and it may equably be apportioned between the 14 series measured.

Taking all probable errors into account, the accuracy of determination of the isotherms may be put at 1 in 1,000.

§ 10. *Discussion of Results.*

(*a*) ***Individual Gases.***—The equation for the isotherm of hydrogen at 0° C., as found by Holborn (*loc. cit.*), is

$$(pv)_B = 0·99918 + 0·8209 \times 10^{-3}\, p_B + 0·3745 \times 10^{-6}\, p_B^2.$$

When converted into our units, this reads

$$pv_A = 0·99938 + 0·6240 \times 10^{-3}\, p + 0·2163 \times 10^{-6}\, p^2,$$

and this agrees very closely with our equation, as will appear from Table XII, wherein are given the pv_A — values at 50, 100, and 200 atmospheres, derived from our equation (W), and from the Berlin one (B), the Berlin value for 200 atmospheres is enclosed in brackets, because the Berlin isotherm really extends only to 100 atmospheres.

Table XII

p	pv_A (W)	pv_A (B)
50	1.0311	1.0311
100	1.0637	1.0640
200	1.1313	(1.1328)

The Leiden equation for the isotherm of hydrogen at 20° C (due to Schalkwijk, *loc. cit.*) is

$$pv_A = 1.07258 + 0.6671 \times 10^{-3}\, d_A + 0.993 \times 10^{-6}\, d_A^2,$$

or, in our form,

$$pv_A = 1.07258 + 0.6351 \times 10^{-3}\, p + 0.206 \times 10^{-6}\, p^2$$

The Amsterdam equation is given by Kohnstamm and Walstra (*loc. cit.*) in the form

$$pv_A = 1.07258 + 0.6763 \times 10^{-3}\, d_A + 0.882 \times 10^{-6}\, d_A^2 + \text{higher terms},$$

and this becomes, in our units,

$$pv_A = 1.07258 + 0.6467 \times 10^{-3}\, p + 0.161 \times 10^{-6}\, p^2$$

Table XIII contains the pv_A values given by our equation and by the Leiden (L), the Amsterdam (A), and the interpolated Berlin equation, the agreement with the Amsterdam equation is not very good.

Table XIII

p	pv_A (W)	pv_A (L)	pv_A (A)	pv_A (B)
50	1.1053	1.1049	1.1051	1.1051
100	1.1384	(1.1382)	1.1389	1.1383
200	1.2055	(1.2079)	1.2084	(1.2066)

Holborn and Otto's equation (*loc. cit.*) for the isotherm of nitrogen at 0° C is

$$(pv)_B = 1.00060 - 0.6072 \times 10^{-3}\, p_B + 5.406 \times 10^{-6}\, p_B^2$$

On conversion into our units, we obtain

$$pv_A = 1.00045 - 0.4614 \times 10^{-3}\, p + 3.122 \times 10^{-6}\, p^2$$

The Leiden equation (Kamerlingh Onnes and van Urk, *loc. cit.*) reads

$$pv_A = 1.00041 - 0.4102 \times 10^{-3}\, d_A + 2.066 \times 10^{-6}\, d_A^2,$$

or

$$pv_A = 1.00041 - 0.4101 \times 10^{-3}\, p + 1.898 \times 10^{-6}\, p^2$$

As stated by Smith and Taylor (*loc. cit.*), the equation of state for nitrogen is given by

$$p = \frac{2{\cdot}92855}{v - \delta}\mathrm{T} - \frac{1623{\cdot}6}{(v + 0{\cdot}2945)^2}, \text{ where } \log_{10}\delta = 0{\cdot}18683 - \frac{0{\cdot}3113}{v}$$

Smith and Taylor themselves reduce this equation to one developed in powers of $1/v_A$, but, since they neglect all terms of higher order than $1/v_A{}^2$, the reduced equation represents a very rough approximation to the original one. By plotting their results (converted to the usual units) on a suitable scale, and selecting the values of pv_A thus found for $p = 100$ and $p = 200$ atmospheres, it is possible to obtain a standard equation leading to values of pv_A which do not differ from those calculated from Smith and Taylor's equation by more than 1 in 1,000 up to 200 atmospheres. In this way we find, at 0° C.,

$$pv_A = 1{\cdot}0006 - 0{\cdot}5910 \times 10^{-3}\,p + 3{\cdot}67 \times 10^{-6}\,p^2$$

This differs considerably from the other equations, and it appears from Table XIV that our values agree reasonably well with the Berlin and Leiden values, but that the Boston results (derived directly from Smith and Taylor's original equation) are much lower. As was pointed out in § 3, there is every reason to suspect the purity of the gas used at Boston, and this suspicion is apparently confirmed by the numerically larger B_p and C_p values obtained, thus indicating the presence of a gas of comparatively high boiling-point.

Table XIV

p	pv_A (W)	pv_A (Ber)	pv_A (Bos)	pv_A (L)
50	0·9840	0·9852	0·9793	0·9846
100	0·9842	0·9856	0·9782	(0·9784)
200	1·0346	(1·0331)	1·0292	(0·9943)

The Leiden equation for the isotherm of nitrogen at 20° C. is

$$pv_A = 1{\cdot}07370 - 0{\cdot}2625 \times 10^{-3}\,d_A + 2{\cdot}500 \times 10^{-6}\,d_A{}^2,$$

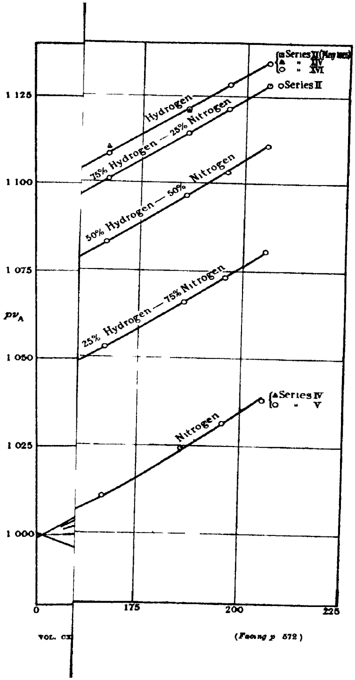
or

$$pv_A = 1{\cdot}07370 - 0{\cdot}2445 \times 10^{-3}\,p + 2{\cdot}114 \times 10^{-6}\,p^2$$

It is possible to interpolate an equation from the Berlin isotherms at 0°, 50°, and 100°, and this is given by

$$pv_A = 1{\cdot}07367 - 0{\cdot}2622 \times 10^{-3}\,p + 2{\cdot}688 + 10^{-6}\,p^2$$

The agreement between both these equations and ours over the ranges covered is good, as may be seen from Table XV.



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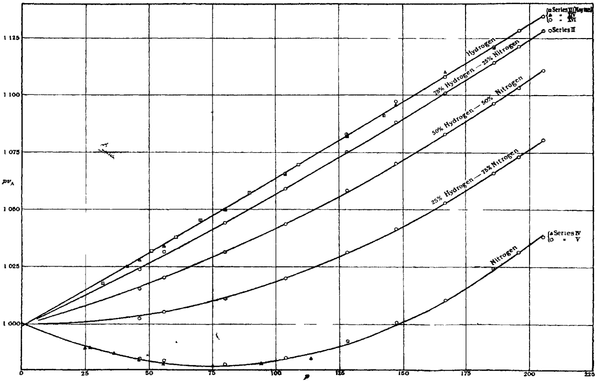

FIG. 5.—Isotherms at 0° C

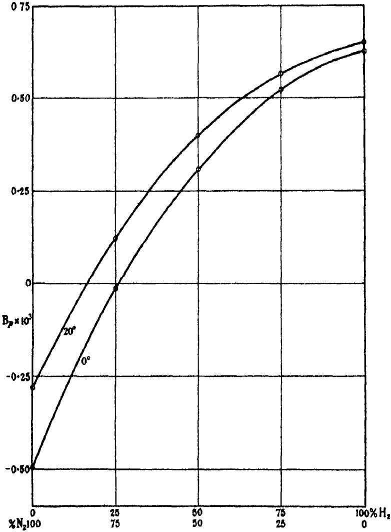
0 75
0·50
0·25
0
$B_p \times 10^3$
20°
0°
-0·25
-0·50
0
%$N_2$100
25
75
50
50
75
25
100%H_2
0

Fig 7

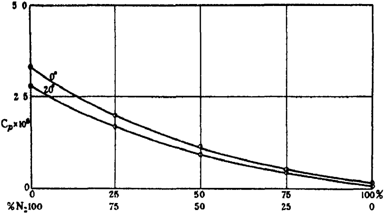

FIG 8

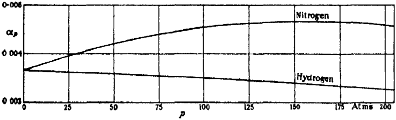

FIG 9.—Expansion Coefficients.

Summary

§ 1. The object of this research is stated.

§ 2. The most accurate determination of the isotherm of hydrogen at 0° C is that effected by Holborn, but this extended only to 100 atmospheres. Schalkwijk's measurement of the isotherm at 20° C up to 60 atmospheres is probably the most exact determination of the kind ever made. Kohnstamm and Walstra extended this isotherm to 1 000 atmospheres, but for several reasons their results are not so accurate.

§ 3. The determinations of the isotherm of nitrogen at 0° C, both by Kamerlingh Onnes and van Urk up to 60 atmospheres, and by Holborn and Otto up to 100 atmospheres are reliable, but the measurements by Smith and Taylor are open to serious objection. The isotherm at 20° C has been directly measured only by Kamerlingh Onnes and van Urk, up to a pressure of 60 atmospheres

§ 4 A description is given of the apparatus employed in this investigation with special reference to the steel piezometer, details of which are somewhat novel

§ 5 The origin and purity of the gases used is discussed

§ 6 The units of pressure and volume adopted are the international atmosphere and the normal volume Isotherms are expressed by developing pv_A in powers of p

§ 7 Tables of the experimental data obtained for the individual gases and three mixtures at 0° and 20° C are reproduced

§ 8 A table of the values of the constants in the equations for the several isotherms is given

§ 9 Sources of errors and their magnitudes are discussed The final accuracy may be estimated at 1 in 1,000

§ 10 The experimental results are compared with those obtained in previous investigations It is shown that there is no justification for assuming the pv_A values for a mixture to be a linear function of the composition, at least when the critical temperatures of the component gases are widely different

For the design of the apparatus and the technique employed in this research I am indebted almost entirely to Prof H Kamerlingh Onnes, in whose laboratory I had the great good fortune to work for a year The glass-blower of this laboratory (Mr H J Welbergen) constructed all the rather complicated glass work, and the fine mechanic (Mr J Pont) was responsible for the construction and assembly of all the instruments (other than those of standard pattern) and fine metal work To my assistants (Messrs H Ryder and J C Johnson) I owe my thanks for their help in the experimental observations and in the computations Finally, I am most grateful to Capt F A Freeth, F R S, for his continual help and encouragement throughout the whole period of construction and determination

The Mobility of Ions in Air Part III —Air Containing Organic Vapours

By Prof. A M Tyndall and L. R Phillips

(Communicated by Prof A P Chattock, F R S —Received April 6, 1926)

The data on mobility of gaseous ions available at present have not led to a satisfactory quantitative theory of ionic structure because of the large number of variables necessarily entering into the formulæ deduced The writers feel that the most fruitful line of experimental attack is to carry out a series of different experiments under conditions chosen so that one or more of these variables may be regarded, at any rate approximately, as unchanged throughout the series The work herein described is an attempt in that direction and deals with the mobility of ions in air containing the vapours of a series of closely related organic substances

It is well known that the presence of water vapour in air causes a reduction in the mobility of the negative ions The effect has recently been studied in detail from small traces up to saturation by one of the writers (A M T) and Mr G C Grindley * Other vapours are also known to be similarly effective Thus Rutherford† showed that alcohol and ether vapour lower the mobility of negative ions in air Przibram‡ found that various saturated organic vapours affect both positive and negative mobilities, though quantitatively his method is not free from objection Wellisch§ found that 10 mm of alcohol or acetone introduced into air at atmospheric pressure caused a reduction in both mobilities, but that 6 mm of ethyl bromide or iodide had no effect

These results with organic vapours are of considerable interest, but the information given by such isolated observations is too incomplete to throw much light upon the problem of the mechanism of the process For this reason the present writers have examined the effect of certain vapours in detail Those specially selected were the lower members of the normal aliphatic alcohol series, chloroform and carbon tetrachloride Isolated observations have also been made in saturated propyl iodide, iso-amyl alcohol and two hydrocarbons, octane and decane

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* Tyndall and Grindley, "Mobility of Ions in Air, Part I" ('Roy Soc Proc ' A vol 110, p. 341 (1926))

† 'Phil Mag,' vol 2, p 219 (1901).

‡ 'Wien Akad Sitzb,' IIA, vol 118, pp 331 and 1419 (1909)

§ 'Roy Soc Proc,' A, vol 82, p 500 (1909)

The method adopted was that given in Part I (*loc cit*) to which reference must be made for details Briefly the method depends upon the production of ions by a series of flashes of α-rays and their subjection to an alternating field of a special kind The conditions are so arranged that when the current arriving at an electrometer is plotted with frequency of alternating field a curve with a sharp peak is obtained, the position of which gives an accurate measurement of the mobility

Experimental Details.

The method was used as a comparative one The current-frequency curves were obtained in dry air containing vapour, and in dry air alone The peak frequencies were compared and the mobility in the alcohol mixture calculated from the value in dry air alone, known from the previous paper

Since only relative values were necessary certain simplifications in the apparatus were possible The mobility box was reconstructed with a fixed distance between the plates and of dimensions more suitable for the introduction of liquids without opening the box The gauze method of eliminating the effect of induction on the electrometer was used

The box was of ⅛ inch brass and of external dimensions 10 5 inches by 10 5 inches by 2 5 inches The roof of the box had a central hole, 1 5 inches diameter and served as the guard ring for the electrometer plate A short vertical tube 3 5 inches long and projecting upwards from this hole was soldered to the roof, and was closed at its top end by an ebonite and sulphur plug This plug supported and insulated the rod from the electrometer plate, which nearly filled the hole The induction gauze was supported and insulated from the roof by four ebonite blocks It was made of zinc drilled with $\frac{1}{16}$ inch holes and was gripped round its edges between two square pieces of $\frac{1}{16}$ inch aluminium The distance between the gauze and the electrometer plate was 1 cm and between the two electrodes 5 cm.

Having dried the box and the air in it by sweeping a current of dry air through it for some hours, the liquid giving the vapour under test had to be introduced into the box without opening it For this purpose a glass funnel which passed through a hole in the roof was filled with the liquid in question Inside the box and underneath the funnel was a metal tray which could be filled with the liquid by opening the stopcock of the funnel After about one hour it was assumed that the vapour inside the box was at the saturated value appropriate to the particular liquid used It is unlikely that any error due to this assumption had any serious effect on the nature of the results obtained

The investigation of the vapour over a range of concentrations presents certain difficulties Air saturated with vapour may be diluted with dry air and then introduced into the box, but if there is any absorption of the vapour by the walls and plates the concentration may have entirely changed before the mobility measurements are completed Equilibrium with the walls might be secured by making up a large volume and passing it slowly through the box, but this is inconvenient These difficulties may be avoided by finding some organic solvent the vapour of which has no appreciable effect on the mobility of air ions Aniline and quinoline, as high boiling-point liquids with low vapour pressure and with no chemical action on the liquids under investigation, were tried, and of these the latter was found to satisfy this test A series of solutions of known molecular concentrations of a given alcohol or other liquid were therefore made in quinoline for insertion in the mobility apparatus Care was taken to insure that the chemicals were as pure and as dry as possible

For a quantitative study it is necessary to know the vapour pressure of these solutions No definite measurements appear to have been made of the vapour pressures of organic substances in non-volatile solvents, but in the present case there does not seem to be any reason to anticipate constant boiling point mixtures, and we may therefore expect the vapour pressure of the substance to be roughly proportional to its percentage molecular concentration, the vapour pressure of quinoline being taken to be negligibly small As a rough test, however, some measurements of the vapour pressures of several methyl alcohol solutions in quinoline were made with a static vapour pressure apparatus The experiments were somewhat crude but the results were in reasonable agreement with this view The vapour pressures given later in the paper are, therefore, calculated on the assumption of proportionality to percentage molecular concentration in quinoline, but if it ever becomes necessary the values can be checked by refined vapour pressure measurements

The procedure was then as follows The mobility was taken in dry air, a weak solution of a given liquid was then poured in, and after about one hour the mobility was retaken The box was then opened at both ends, the tray of liquid taken out and ordinary room air blown through the apparatus to remove the vapour After cleaning, the tray was reinserted ready for the next solution, the box was closed and dry air blown through it for several hours Tests showed that it was possible in this way to regain the original value of mobility obtained before the vapour was present The procedure was then repeated for other solutions in order of increasing concentration up to saturation

Before passing on to the solutions of another liquid it was very important to remove all traces of the vapour previously used This was not always easy because the last concentration employed was the pure liquid and some condensation may have occurred on the walls In several cases it was necessary to take the apparatus down and heat the box in front of an electric radiator in a stream of air The investigation of the solutions of a given liquid was never started until, with pure quinoline in the tray, the peak frequency was practically that given originally in dry air

Results

The results in the series of alcohols are shown most conveniently in graphical form Figs 1 and 2 show the variation of mobility of negative and positive ions respectively in air (at room temperature and pressure) with partial pressure of added vapour The curves relate to the first five normal alcohols of the

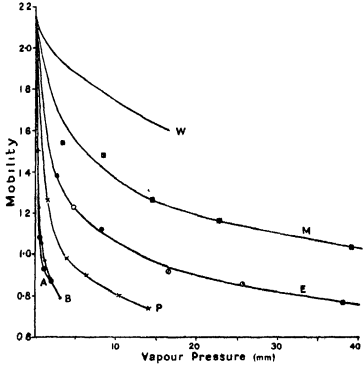

FIG. 1 —NEGATIVE IONS

W = Water
M = Methyl Alcohol.
E = Ethyl Alcohol
P = *n*-Propyl Alcohol.
B = *n*-Butyl Alcohol.
A = *n*-Amyl Alcohol.

series and to octyl alcohol (one point only marked + and lying practically on the curve for amyl alcohol) In fig 1 the results for water vapour obtained in the previous paper are also inserted for comparison

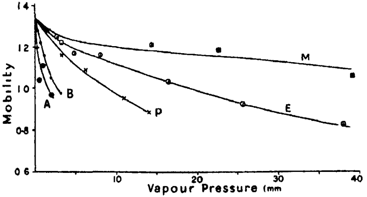

FIG 2 —POSITIVE IONS

Reference letters the same as in fig 1

Measurements have been made over the whole range up to and including saturated vapour of pure liquid though the scale does not permit of the inclusion in the graph of the values for the highest pressures of methyl alcohol

The curves in all cases show that a drop in mobility occurs with rise of vapour pressure In the case of negative ions there are two striking features (1) the steep gradient at low concentration (2) the increase in this gradient as one proceeds up the alcohol series from methyl alcohol to octyl alcohol For instance in amyl alcohol the curve is so steep that the vapour at one millimetre pressure reduces the mobility of negative ions from 2 15 to 0 93

The vapour pressure of octyl alcohol at room temperature is not known but from Ramsay and Young s relationship and other data for homologous substances it may be estimated to be of the order of 0 3 mm This reduces the mobility of negatives from 2 15 to 1 50

In the case of positive ions the initial steep gradient is far less marked There is, however a general drop in mobility with rise of vapour pressure and the several alcohols follow the same sequence

At the same time caution must be observed in using the positive results It is now well known that more than one type of positive ion is possible in air and until measurements have been made in vapours with ions of different ages we cannot say definitely what was being measured Fig. 3 shows a typical pair of peaks selected from many obtained for positive and negative ions, this

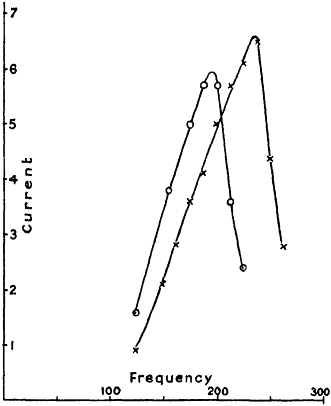

Fig. 3 —Typical Peaks

○ = Negative Ions. × = Positive Ions

particular one being for propyl alcohol of vapour pressure 6 45 mm The spreads of the two curves are comparable with one another, suggesting that the majority of the positive ions are of one kind The life of these ions was about 0 05 sec

For methyl alcohol and also ethyl alcohol at low concentration the experimental points show irregular deviations from the smoothed graph This may be due to an occasional trace of water vapour creeping in inadvertently

Fig 4 shows the results of chloroform and carbon tetrachloride, the scale of the abscissæ being changed to include the high vapour pressures which are possible with these substances. The negative curves are of the same type as

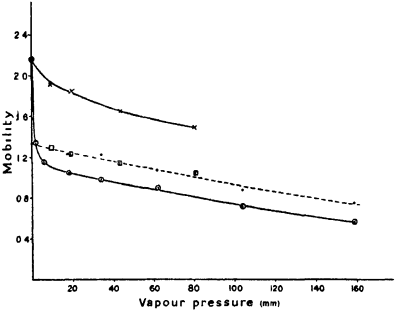

FIG. 4.—RESULTS FOR CHLOROFORM AND CARBONTETRACHLORIDE.

⊙ $CHCl_3$ — Negative Ions.
× CCl_4 — Negative Ions.
• $CHCl_3$ — Positive Ions.
□ CCl_4 — Positive Ions.

those for alcohols, but the two positive curves appear to have no initial drop and approximately coincide.

For special reasons single measurements at saturation pressure in air have been taken for iso-amyl alcohol, propyl iodide, octane, decane, and for the mixed saturated pressures of amyl alcohol and water. The significance of the results relative to those for the alcohols will be discussed later. Table I is a summary of all the data obtained.

In passing it may be noted that at saturation the mobilities of negative ions for the first four alcohols only differ by a few per cent, although the pressures range from 3 mms. to 75·5 mms. We are not able to state whether or not this is more than a coincidence.

Table I

Vapour	Molecular percentage.	Vapour pressure in mm	Mobility −	Mobility +
Methyl alcohol CH_3OH	4 24	3 33	1 54	1 22
	10 6	8 50	1 48	1 16
	18 0	14 5	1 26	1 21
	29 0	22 70	1 16	1 19
	48 7	39 10	1 03	1 06
	74 0	57 8	0 87	0 92
	100	75 5	0 78	0 80
Ethyl alcohol CH_3CH_2OH	6 22	2 74	1 38	1 25
	11 70	4 90	1 23	1 17
	22 0	8 22	1 12	1 16
	44 0	16 50	0 92	1 03
	66 0	25 7	0 86	0 92
	100 0	38 0	0 77	0 83
n Propyl alcohol $CH_3(CH_2)_2OH$	10 7	1 55	1 26	1 28
	29 5	3 94	0 98	1 16
	43 8	6 45	0 90	1 09
	71 0	10 35	0 80	0 95
	100 0	14 20	0 74	0 88
n Butyl alcohol $CH_3(CH_2)_3OH$	11 1	0 40	1 22	1 28
	20 2	0 73	1 05	1 22
	34	1 06	0 97	1 16
	56	1 79	0 88	1 05
	100	3 15	0 79	0 98
n Amyl alcohol $CH_3(CH_2)_4OH$	26 4	0 61	1 10 ?	1 04 ?
	51 8	1 09	0 93	1 11
	100	2 10	0 87	0 97
n-Octyl alcohol $CH_3(CH_2)_7OH$	100	0 3 ?	1 50	1 30
Chloroform $CHCl_3$	1 44	2 1	1 34	1 34
	4 3	6 2	1 16	1 34
	12 7	18 4	1 05	1 22
	22 6	34 2	0 98	1 22
	42 1	61 9	0 90	1 07
	74	104 0	0 71	0 87
	100	159	0 56	0 74
Carbon-tetra chloride CCl_4	11 75	9 4	1 92	1 29
	25	19 5	1 88	1 23
	54 3	43 5	1 64	1 14
	100	80 2	1 52	1 05
n Propyl iodide $CH_3(CH_2)_2I$	100	30 0	0 81	0 93
Iso amyl alcohol	100	1 88	0 73	0 96
n Octane $CH_3(CH_2)_6CH_3$	100	10·0	1 81	1 14
Decane (di-iso amyl)	100	2 3	1 96	1 38
Amyl alcohol	100	2 1	1 14	1 07
+ Water	100	14 0		

Discussion of Results.

The sudden drop in the mobility of negative ions in air owing to small traces of alcohol and other organic vapours is difficult to explain except on the supposition of a cluster theory Loeb[*] has recently shown that curves of exactly the same type are obtained in hydrochloric acid-air mixtures, and has attributed the effect to a labile cluster of HCl molecules concentrated in the neighbourhood of the ion owing to the high dielectric constant of this gas.

In discussing the results it is necessary to examine the relative importance of the various factors which determine the mobility of a cluster ion * As a preliminary we may consider the nature and formation of a cluster If the work required to separate to infinity a neutral molecule and an ion which are at a distance r from one another is $W(r)$ then according to Boltzmann s theorem the probability that a neutral molecule shall be found in an element of volume at this distance is proportional to $e^{W(r)/kT}$ where k is the usual Boltzmann constant and T the temperature

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[*] 'Proc. Nat. Acad. Sci' (Washington) (January, 1926).

The degree of aggregation round the ion will depend on the affinity between the ion and the neutral molecule and this in turn will depend upon the magnitude of (1) any permanent electric doublet that the molecule may possess (2) an induced electric doublet due to the relative displacement of its electronic and nuclear charges in the field of the ion Due to (1) the function $W(r)$ falls off according to the inverse square law and due to (2) according to the inverse fourth power law Even when W is large for small values of r (say 2 or 3 Å) it rapidly diminishes at greater distances particularly if the molecules under consideration have no permanent moment Whether therefore we regard the cluster as labile (as Loeb does) or not there does not appear to be any strong evidence for supposing that it is equivalent statistically to a layer more than one molecule thick For simplicity then we shall assume the molecules to be held in one layer in virtual contact with the ion i e in equilibrium under the joint action of their mutual repulsive and attractive forces

We can now enumerate the factors determining the mobility of an ion In the simplest case these are at least four in number —

(1) The density of the gas (ρ) In most of the substances examined this may be taken to be constant throughout at any rate at the lower concentrations

(2) The distance between the centres of a molecule and a cluster at collision (σ) For instance in Langevin s treatment† this enters as a term proportional to $1/\sigma^2$

(3) The mass of the ion (M) and molecule (m) Again in Langevin s formula these enter as a term $\left(1+\frac{m}{M}\right)^{\frac{1}{2}}$ which for any fully formed cluster approximates to unity That this is probable is shown by several observations among the above results For instance the negative curve for chloroform (mol wt 120) lies wholly above that for propyl

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* We wish to acknowledge with thanks the help we have gained through a discussion of this section with Dr Lennard Jones.

† For an analysis of Langevin s theory *see* Hassé Phil Mag. vol 1 p. 139 (1926)

alcohol (mol wt 60), and above the greater part of that for ethyl alcohol (mol wt 42) Secondly, saturated propyl iodide (mol wt 163) gives a negative mobility 0 8 which is higher than 0 74 obtained for saturated propyl alcohol (mol wt 60) at *half* the vapour pressure This argument is not conclusive because the other factors may be different, but it may clearly be said that the mass factor is not a dominating one

(4) A term which for convenience we will call the clustering coefficient "C," and which will depend upon the combined magnitudes of the permanent and induced doublets in the molecule

Following upon earlier work by Debye, J J Thomson and Gans, C P Smyth[*] has calculated the electric moment of the permanent doublet for a large number of substances The numbers he obtained for the substances dealt with in this paper are given in Table II

Table II

Substance	Electric moment $\mu \times 10^{18}$	Substance	Electric moment $\mu \times 10^{18}$
Water	1 98	Propyl iodide	$>1\ 31<1\ 62$
Methyl alcohol	1 78	Chloroform	1 25
Ethyl alcohol	1 85	Carbontetrachloride	0 48
Propyl alcohol	1 98	Octane	0 0
Butyl alcohol	2 06	Decane	0 0
Amyl alcohol	2 15		

The values of the induced moment in unit field have been calculated for certain atoms and molecules by Born and Heisenberg,[†] Fajans and Joos [‡] For instance, the former give to HCl the value $2 \cdot 5 \times 10^{-24}$ The problem is a complicated one, but on certain assumptions we can deduce the relative orders of magnitude of the two moments Taking the case of the alcohols we will assume (1) that the permanent and induced moments are located in the OH group and approximately at the same distance from the ion treated as a point charge, (2) that the proportionality of induced moment to the average field still holds in the intense divergent field near the ion (this cannot be strictly true), (3) that the induced moment in the OH group for which no data are available is not likely to be very different from that in HCl Taking therefore the value 2×10^{-18} for the permanent moment and $2\ 5 \times 10^{-24}$ for the induced moment in unit field we find that the ratio of the force f_p exerted upon an electron by the permanent doublet to that f_i exerted by the induced doublet at a distance of r Å is given by $f_p/f_i = r^3/6$

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[*] C. P. Smyth, 'Phil Mag,' vol 45, p. 849 (1923); 'J.A.C.S.,' vol. 46, p. 2151 (1924), etc

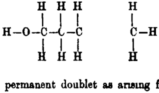
[†] 'Zeit. f. Physik,' vol 23, p. 388 (1924)

[‡] 'Zeit. f. Physik,' vol. 23, p. 1 (1924).

When r is of the order of a few Angström units the forces are then of the same order of magnitude

One might argue that this detailed treatment might be dispensed with and that we might take the known values of dielectric constant as a measure of the clustering coefficient But apart from the fact that the dielectric constant data are only known for the weak fields of ordinary laboratory practice whereas we are considering intense fields it appears to us that the resultant moment may depend upon the sign of the ion dealt with

If we consider the alcohol molecule to be of the chain type shown for the higher solid members by X rays, its structure may be expected to be of the form—



$$\mathrm{H{-}O{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\qquad\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H}$$

If we now regard the permanent doublet as arising from a positive charge on the hydrogen and a negative on the oxygen of the OH group this end of the molecule will be attracted and on the average will present itself to a negative ion The induced moment will act in the same direction and the resultant force on the molecule will be due to the sum of the two The force however between a positive ion and a *similarly orientated* molecule will be due to the difference between them Some re orientation of the molecule will therefore take place with a resultant reduction in C for a positive ion Though this taken alone does not explain all the facts it may account for the smaller drop in mobility of the positive ions which the curves show *

Considering now these four factors (ρ σ M and C) for the particular case of the several alcohol mixtures we see that we may take ρ as a constant and the mass term as unity The important factors are therefore σ and C In general unless the cluster is fully formed of alcohol molecules σ will depend upon C

From Smyth s figures for the permanent moment and on general grounds we should expect that C would not vary very much in passing from a short chain, CH_3OH, to a long chain, $CH_3(CH_2)_4OH$ If then we regard C as approximately constant for the series, we are left with σ as the factor determining the relative mobilities through the series. Now, since σ will increase the mobility will therefore drop as the length of the chain increases This is precisely what is observed in the case of the four lower alcohols The following table shows the mobilities in air containing alcohol vapours all at the same partial pressure, 2 mms

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* Since this paper has been prepared a copy of the Journal of the Franklin Institute March, 1926 has come to hand, in which Loeb discusses the effect of permanent and induced di poles, and in particular advances an interesting qualitative explanation of the difference between positive and negative gaseous mobilities in terms of the highly divergent fields close to an ion and the discrete electrical structure of the molecule

Alcohol vapour	Mobility	
	−	+
Methyl	1 77	1 27
Ethyl	1 46	1 25
Propyl	1 15	1 23
Butyl	0 87	1 05
Amyl	0 87	0 97

The value for the negative ion in amyl alcohol, the last of the series, at its saturation value 2 mm , is approximately the same as that of butyl alcohol, but the general argument is not necessarily invalidated for the following reasons —

(1) It is doubtful how far the value of the vapour pressure of this alcohol obtained in the year 1882 can be regarded as accurate, since at that time the technique of removing small amounts of impurity was not fully developed

(2) The value of each mobility has not reached a limit of approximately constant slope We are not therefore justified in the assumption made above, that the cluster is entirely made up of alcohol molecules In the case of octyl alcohol for instance, at the saturation pressure (about 0 3 mm), the point obtained is still on the very steep portion of the curve at a mobility of 1 50.

Clearly no quantitative treatment is possible at this stage , but it is safe to say that the early steep slope and its subsequent falling-off, and the relative shapes of the curves as one ascends the series, are in agreement with the view that, due to their greater total electric moment, alcohol molecules rapidly replace air molecules in the cluster as the concentration of alcohol increases ; and that the relative effects of the several members of the series depend mainly upon the relative values of σ for the cluster so formed

When we pass from one substance to another which is not in the same homologous series the problem is more complicated, as we shall in general change both

C and σ. In certain cases, however, qualitative results may be deduced. For instance, if we pass from a normal alcohol to a normal hydrocarbon by the substitution of a hydrogen atom for the OH group at the end of the chain we may expect a marked reduction in C. Thus Smyth's figures give no permanent moment in hydrocarbons and there is reason to think that the induced moment is also small. The experimental results shown in Table I for octane and decane are in marked agreement with this view. Thus 10 mm. vapour pressure of the long chain molecules of octane only reduces the mobility of the negative ions to 1.81 as compared with 0.8 for 10 mm. of propyl alcohol with a molecule of roughly half the length. Decane at saturation has still less effect (1.96) though the difference between the two hydrocarbons may be mainly due to the difference in their vapour pressures.

Again according to Smyth substituting iodine for the OH group in propyl alcohol should decrease the permanent electric moment. If this is an important part of C propyl iodide should have less effect on mobility than propyl alcohol assuming the molecular dimensions to be roughly the same for both. This is again in accordance with experiment since a pressure of 30 mms. pressure of propyl iodide does not reduce the mobility so much as 14 mms. of the corresponding alcohol.

Finally an interesting comparison may be made between chloroform ($CHCl_3$) and carbontetrachloride (CCl_4). Smyth's estimates of permanent moment are 1.25 and 0.48 respectively and other things equal we should therefore expect the latter to have less effect than the former on mobility. In agreement with this view fig. 4 shows the negative curve for carbontetrachloride lying wholly above that for chloroform in spite of the fact that carbontetrachloride must have a somewhat bigger molecule. The reason for the coincidence of the two positive curves and the apparent absence of any initial drop is however not clear but as mentioned above much more information is required about the positive ions before the results for them can be properly analysed.

Mixtures of two Vapours

While the foregoing is entirely consistent with the cluster theory we have looked for some test which would be still more strongly in its favour. In our opinion this has been obtained in a series of measurements we have made in air containing (1) water only, (2) amyl alcohol only, and (3) the vapours mixed. Reference to the previous data for these two vapours separately shows that 2 mms. pressure of amyl alcohol reduces the mobility from 2.15 to 0.88, while 14 mms. of water only reduces it to 1.60. Readings were taken first with a tray of alcohol in the box, the air being dry, and then with a tray of water inserted as well This procedure was alternated several times The sets of readings for negative ions are shown in fig 5 (A for alcohol, and B for alcohol and water),

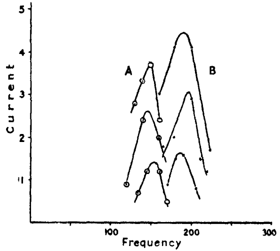

Fig 5

the zero for the ordinates being varied for each pair for clearness The mean value of the peak frequency gives the mobility in each case The curves show beyond doubt that the mobility is greater in the mixed vapour than it is in the alcohol alone, the mean values being 0 90 and 1·14 respectively

Now this result is in entire agreement with the cluster theory The probability of a molecule of amyl alcohol finding itself in virtual contact with the ion is a function of $e^{W_a/kT}$, where W_a is the work done in separating them to infinity The probability in the case of a water molecule is similarly $e^{W_w/kT}$ From the data for electric moments given above we may assume that W_a and W_w are at least of the same order of magnitude If, therefore, water vapour is introduced into the air-alcohol mixture, then for statistical equilibrium some of the alcohol molecules will be replaced by water molecules Since, however, the water molecules are smaller than the long chain alcohol molecules, the statistical effect is a reduction in the effective diameter of the cluster and consequently a rise in mobility This is precisely what is observed experimentally

Summary

Measurements of the mobility of ions have been made in air containing organic vapours over a range of concentration extending up to saturation In every case a reduction in mobility is produced by the addition of vapour though the amount depends upon the constitution of the vapour and the sign of the ion

The gradient of the mobility vapour pressure curve for the negative ion is in general steep at low concentrations but falls off later In the case of the homologous series of normal aliphatic alcohols the steepness increases as one ascends the series, the effect of the higher alcohols being very striking Similar effects have been observed for the positive ion, but the initial drop in mobility is much less marked Experiments with ions of different ages are necessary however before the results with positive ions can be properly analysed The influence of chloroform and of carbontetrachloride vapours has also been studied in detail and isolated observations made at saturation in propyl iodide and in the long chain hydrocarbons, octane and decane

The factors entering into the cluster theory of gaseous ionic structure are examined with special reference to these results It is suggested that the relative effects of the various vapours depend upon (1) a " clustering coefficient " determined by the combined effect of any permanent electric moment and an induced electric moment in the neutral molecule , (2) the " effective diameter " of the cluster Of the twelve vapours examined, every one gives results consistent with this view In fact it seems impossible to explain the results without resource to some form of cluster theory This is confirmed by the fact that the effect of adding saturated water vapour to a saturated amyl alcohol-air mixture is to *raise* the mobility Owing to the replacement of some alcohol molecules by water molecules in the cluster this result follows as a natural consequence from the theory as formulated

Our thanks are due to Mr G C Grindley for assistance given at various stages of the investigation, and to the Colston Research Society of the University of Bristol for a grant in aid

On the Drag of an Aerofoil for Two-Dimensional Flow.

By A Fage, A R C Sc , and L J Jones, of the Aerodynamics Department, National Physical Laboratory

(Communicated by H Lamb, F R S —Received April 12, 1926)

Introduction

(1) According to modern aerofoil theory, the drag of an aerofoil of finite span is compounded of two parts, one a profile drag associated with the shape and attitude of the section, and the other an induced drag connected with the variation of lift along the span The magnitude of this induced drag can be determined when the forces acting on the aerofoil are known As the span increases, the profile drag per unit length approaches a limiting value, whereas the induced drag becomes relatively smaller, because of the more uniform distribution of lift, and would disappear completely if the span were infinite. The present paper* deals exclusively with the profile drag of an aerofoil of infinite span, or, in other words, the drag for two-dimensional flow

L W Bryant and D H Williams† have shown from explorations of velocity in the wake of an aerofoil mounted between the walls of a wind tunnel, that the flow around the central part of the aerofoil, at a sufficient distance from the walls, is, for all practical purposes, two-dimensional In an Appendix to the above paper, Prof G I Taylor shows that there is good reason to believe, on theoretical grounds, that the drag of an aerofoil can be determined with good accuracy from observation of total head losses in the wake, provided that these observations are taken in a region where the velocity disturbances are relatively small, that is, at a sufficient distance behind the aerofoil The present investigation has been undertaken to examine experimentally this method of measuring drag, and also to throw light, in a general manner, on some characteristics of the wake The experiments were made on an aerofoil of 0·5 foot chord mounted in a 4-foot wind tunnel, with small clearances between the tips and the tunnel walls (0 15 inches) Preliminary observations of total head showed that the wake was uniform along the span, except in the neighbourhood of the walls where it opened out appreciably To establish the fact that the drag could be determined from the total head losses observations for 0° incidence—were taken in the wake at several sections chiefly near the aerofoil tips The drag of the entire aerofoil was then estimated from the integral along the span of the losses at each section This value of the drag was found to be in close agreement with that measured directly on a balance and it was concluded that the drag for two dimensional flow could be estimated with good accuracy from the measurements of the total head losses in the wake behind the median section

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* The work described in this paper was carried out in the Aerodynamics Department of the National Physical Laboratory, and permission to communicate the results was kindly granted by the Aeronautical Research Committee.

† "An Investigation of the Flow of Air around an Aerofoil of Infinite Span," 'Phil. Trans. Roy Soc ,' Series A, vol. 225.

Observations of the normal components of the pressure around the median section of the aerofoil have been made and it has been estimated that in the neighbourhood of minimum drag they account for about 80 per cent of the total drag For this particular aerofoil therefore the surface tractions contribute about 20 per cent of the total drag

Included in the paper is a comparison between the drag for two dimensional flow predicted by the Prandtl theory from force measurements on an aerofoil of rectangular plan form the ratio of span to chord being 6 1 and that estimated from the total head losses in the wake the agreement is close except at large incidences where the discrepancy is of the order of 10 per cent

Finally observations of pressure and velocity taken in the wake at some distance behind the aerofoil (0 68 chord) show that most of the total head losses can be accounted for by a decrease of velocity and that the pressure does not differ appreciably from that measured in the surrounding stream

Drag estimated from the total head losses in the wake

(2) Prof Taylor* has shown from considerations of momentum that if D be the drag per unit span of an aerofoil in two-dimensional flow then

$$D = \int_c H \quad l \quad ds + \rho \int_c \left(muv + \frac{lu^2}{2} - \frac{lv^2}{2} \right) ds,$$

where the integration is taken around a closed contour enclosing the aerofoil and

H ≡ total head,

ρ ≡ density of fluid

l and *m* ≡ the direction cosines of the normal to the element *ds* of the contour

u and *v* ≡ components of the velocity relative to the undisturbed wind (The axis of *x* is in the direction of the undisturbed wind.)

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* *Loc cit*

At a sufficient distance from the aerofoil, the second expression contains only second order terms of the small quantities u and v, so that $D = \int_{s} H \, ds$ approximately, when the integration is taken along a line passing through the wake at right angles to the undisturbed wind direction.

(3) To test this theoretical expression for the drag, experiments were made with an aerofoil of a 0·5 foot chord mounted, with small clearances (0·15 inch), between the walls of a 4-foot wind tunnel. The shape of the aerofoil section is shown in fig. 1. The speed of the undisturbed wind was 60 feet per second.

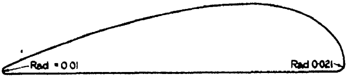

Fig. 1.

The observations of total head were made with a small instrument suitable for use in a two dimensional flow. The head of this instrument was composed of three small tubes mounted in the same plane, with the side tubes at 60° to the central tube. The total head was measured at the central tube, which was pointed into the direction of the relative wind by rotating the instrument until the pressures in the outside tubes were equal.

Explorations of total-head losses were made in the wake of the median section, at distances 0·68 and 1·53 chords behind the trailing edge, and with the aerofoil at incidences −8·05°, −4·05°, −0·05°, 3·95°, 7·95° and 14·95°. These results are given in figs. 2 and 3, where values of the total head losses, expressed as absolute coefficients $\left(\frac{H_0 - H}{\rho v^2}\right)$, are plotted against z, *i.e.*, the normal distance measured, in chords, from a line drawn through the trailing edge parallel to the undisturbed wind direction. The positive direction of z is measured away from the under-surface of the aerofoil.

The curves of figs. 2 and 3 need little explanation; they show that the wake has a minimum extent in the neighbourhood of minimum drag (about 0°), and that it opens out with the passage downstream. Values of the integral of the total-head losses in the wake, *i.e.* $\frac{1}{\rho v^2}\int (H_0 - H)\, dz$, estimated from the areas of these curves are given in Table I.

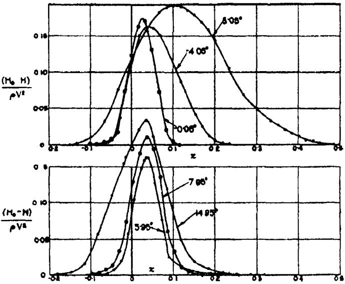

FIG 2 —Total Head Losses in the Wake 0 68 Chord behind Trailing Edge.

Total Head Losses n the Wake 1 53 Chords behind Trailing Edge

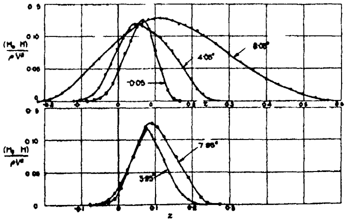

FIG 3 —Total Head Losses in the Wake 1 53 Chords behind Trailing Edge.

Table I —Values of $\frac{1}{\rho v^2}\int(\mathrm{H}_0 - \mathrm{H})\, dz$

Angle of Incidence Degrees	Section 0 68 chord behind trailing edge	Section 1 53 chords behind trailing edge
8 05	0 0524	0 0494
−4 05	0 0224	0 0233
−0 05	0 0132	0 0131
+0 14	—	0 0144
3 95	0 0132	0 0135
7 95	0 0178	0 0164
14 95	0 0330	—

The two series of values of $\frac{1}{\rho v^2}\int(\mathrm{H}_0 - \mathrm{H})\, dz$ are seen to be in fairly satisfactory agreement, also, the small differences do not appear to follow any systematic variation with incidence, the value at 0 68 chord being sometimes greater and sometimes less than that at 1 53 chords The results indicate, therefore, that the flow at these two distances behind the aerofoil is comparatively steady

(4) It is now necessary to see whether the average values of $\frac{1}{\rho v^2}\int(\mathrm{H}_0 - \mathrm{H})\, dz$, where z is measured in chords, give with satisfactory accuracy, the drag coefficients, k_{D},* for two-dimensional flow For this purpose, an exploration of total-head losses along the entire span of the aerofoil has been made, and the drag estimated from these observations compared with that measured directly on a balance In these experiments, the aerofoil was mounted horizontally in the centre of the wind tunnel at an incidence of 0 14°, with clearances at the walls of about 0 025 chord The explorations of total-head losses were made in planes parallel to the tunnel wall, at distances from the aerofoil tip (y_1), measured in chords of 0 10, 0·20, 0 45, 0 95 and 4 0 (median section)

Preliminary measurements behind an aerofoil tip showed that the wake was modified by the influence of the wall, and in such a manner that the losses of total-head increased continuously with the distance downstream. It was therefore necessary to take the observations in this region close to the aerofoil, and to estimate the losses from the difference between readings taken near the leading and trailing edges These results, although uncertain, are considered to be sufficiently accurate for the present purpose.

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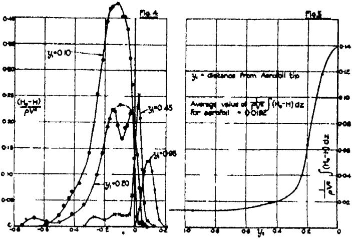
* The non-dimensional coefficient k_{D} is obtained by dividing the drag per unit length by the product of the density, the chord and the square of the wind speed.

The observations of the total-head losses are given in fig 4 These curves show that the wake opens out considerably towards the tip Values of



Figs 4 and 5 —Total Head Losses in the Wake of Aerofoil Tip

$\frac{1}{\rho v^2}\int(H_0 - H)\,dz$, estimated from the areas of the diagrams in fig 4, are plotted in fig 5 The curve down through these points shows that the value of $\frac{1}{\rho v^2}\int(H_0 - H)\,dz$ is practically uniform from the centre part of the span (0 0132 approximately) to about 0 8 chord from the tip, and then increases, at first slowly and afterwards very rapidly, towards the tip The average value of $\frac{1}{\rho v^2}\int(H_0 - H)\,dz$ for the entire aerofoil was found to be 0 0192

(5) The direct measurements of drag, for incidences ranging from −7° to 13°, were made in the usual manner, with the aerofoil supported horizontally on wires These results have been plotted in fig 6, and a dotted line drawn through the points Included in the same figure is a line drawn through the values of $\frac{1}{\rho v^2}\int(H_0 - H)\,dz$, measured at the median section A comparison between these two curves shows that the magnitude of the tip effect increases with incidence, and so with lift At an incidence of 0 14°, the measured drag coefficient is seen to be 0 0186, a value which is in close agreement with that estimated from the integral along the span of the total-head losses in the wake (0 0192).

(6) The conclusions to be drawn from the experiments of sections 4 and 5 are, therefore, that the flow over the central part of the aerofoil is closely two-dimensional, and also that the value of the drag coefficient, k_D, can be estimated with good accuracy from the integral of total-head losses in the wake, given by $\frac{1}{\rho v^2}\int (H_0 - H)\, dz$, where z is measured in terms of the chord. It will be noticed that attention has been confined, in the above experiments, to two-dimensional flow below the critical angle, *i.e.*, the incidence where the lift coefficient has a maximum value The reason for this limitation in the scope of the investigation is that the present method of measurement of total-head losses would be unsuitable for the flow in the neighbourhood of, and above, the critical angle

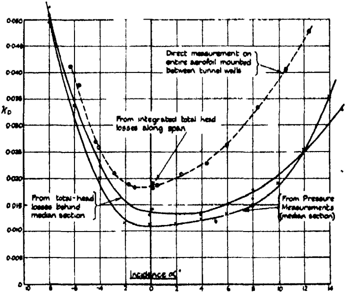


Fig 6.—Profile Drag.

Drag due to the normal components of pressure.

(7) Since the resultant pressure at any point on an aerofoil in a viscous fluid, such as air, does not act normal to the surface, we may regard the drag as compounded of two parts, one due to the normal components of pressure and

the other to the surface tractions. To determine the magnitudes of these two parts, experiments have been made to measure the normal components of pressure around the median section of the aerofoil. The contribution of these pressures towards the drag was then determined from an integration taken around the contour of the aerofoil section. The remainder of the drag is the part due to surface tractions.

In these experiments, the aerofoil was mounted vertically on a turntable fixed to the floor of the tunnel, and to allow a close estimate of the drag, a large number of pressure observations were taken. To obtain accuracy of shape and to permit a large number of holes at the nose, the central part of the aerofoil —span about 8 inches— was cut from cast aluminium. The remainder of the aerofoil was shaped from wood. Close spacing of the holes at the nose was arranged by staggering them in three parallel rows, the two outer rows being displaced about 0·02 chord from the median section. The holes in each row were spaced about 0·024 chord apart, so that the observations at the nose were taken at distances around the section of about 0·008 chord. The holes at the nose, 24 in number, were drilled through the solid aluminium and connected with an inner passage running parallel to the span, and when the pressure was not being measured they were plugged with plasticine. The remainder of the holes were bored in a separate tube let in flush with the surface and were covered *with thin paper discs glued to the surface*. The total number of observations taken around the section was 39, of which 20 were on the upper surface. The normal component of pressure was measured on a 26-inch Chattock Tilting Gauge, against the pressure of the undisturbed wind. The observations were taken at a wind speed of 60 feet per second at incidences ranging in steps of 2° from −8·05° to 19·95°.

(8) The values of the drag coefficient, k_D, were estimated in the standard manner from the pressure observations. At the outset, the coefficients of the forces parallel to and normal to the chord, k_x and k_y, were determined from the areas of the diagrams obtained when the pressure coefficients were plotted on bases representing the maximum thickness and the chord respectively. The values of k_D were then determined from the algebraic sum of the components of k_x and k_y in the undisturbed wind direction, *i.e.*, from $(k_y \sin \alpha - k_x \cos \alpha)$, where α is the angle of incidence. It was found that k_D was often small compared with either $k_y \sin \alpha$ or $k_x \cos \alpha$. The values of k_D are therefore more uncertain than those of either k_y or k_x, although, fortunately, only slightly so in the neighbourhood of minimum drag. The number of pressure observations taken around the section was found to be sufficient to define fairly clearly

the shape of the pressure diagrams, and it is considered that any uncertainty due to this cause does not exceed 2 per cent If this be the case, the uncertainty in the values of k_D will not exceed 5 per cent , at incidences below 4° At higher incidences the uncertainty will probably be greater and may be as high as 10 or 15 per cent in the neighbourhood of the critical angle The value of k_D estimated from the pressure observations, and also from the total-head losses, are plotted in fig 6, and curves are drawn evenly through each set of points It is seen that in the region of minimum drag the normal components of pressure account for about 80 per cent of the drag

Drag due to Surface Tractions

(9) Except near the stall, where both sets of experimental observations are uncertain, there is a nearly constant difference between the full lines of fig 6 This difference represents the drag coefficient due to surface tractions and has an average value of 0 0030 in the neighbourhood of minimum drag Surface tractions contribute, therefore, about 20 per cent of the minimum drag

It follows, since the perimeter of the aerofoil section can be taken, with sufficient accuracy, as equal to twice the chord, that the average intensity, per unit area, of the drag components of the surface tractions is equal to 0 0015ρv^2 It is of interest to compare this value with that for a flat plate, at zero incidence, in a uniform wind The comparison is, of course, not valid on physical grounds, because owing chiefly to the curvature and large velocity gradient at the nose, the conditions of flow are different A sounder comparison, but one not possible with the present method of measurement, would be between the value for a flat plate and the average intensity, per unit area, of the surface tractions on the aerofoil, instead of the drag components of these forces For the purpose of comparison, the value of the surface friction measured by Dr T. E Stanton* and Miss D Marshall on a long flat plate of width 0 5 feet and length 16 feet will be taken These experiments show that when account is taken of the lateral disturbed motion along the edge of the plate, the intensity of surface friction is constant along the plate and equal to 0 00188 ρv^2 at a wind speed of 30 feet per second The average intensity of the drag components of the surface tractions on this aerofoil is therefore of the same order of magnitude as that of the surface friction on a flat plate (actually 20 per cent less)

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* "On the Effect of Length on the Skin Friction of Flat Surfaces." 'Trans. I N A.'

Prediction on the Prandtl Theory

(10) In an earlier paper,* which contains an account of experiments made on an aerofoil of identical section, it is shown that the drag for two-dimensional flow predicted on the Prandtl theory from pressure measurements at the median section of a rectangular aerofoil having a finite span is in close agreement with that measured at the median section of an aerofoil mounted between the walls of a 7 foot wind tunnel A similar comparison will now be made for force measurements on the aerofoil The lift and drag coefficients measured on the rectangular aerofoil (span = 6 chords) have been taken from the earlier paper and are given in Table II below Corrections $(0 \cdot 48\mathrm{K}_L)^\circ$ on incidence and $0 \cdot 0084\mathrm{K}_L{}^2$ on drag have to be applied to these values, to allow for the interference of the tunnel walls The characteristics for two-dimensional flow are then deduced from these corrected observations by subtracting $(7 \cdot 22\ \mathrm{K}_L)^\circ$ from the incidence and $0 \cdot 112\ \mathrm{K}_L{}^2$ from the drag † These predicted values of k_D are given in Table II The values in the adjacent column headed "Experimental" are those estimated from the total-head losses and have been taken from the appropriate curve of fig 6 The agreement between the two series of values is close, except at high incidences, where the accuracy of measurement, in both cases, is somewhat uncertain It appears then,

Table II

Incidence Degrees	Rectangular Aerofoil Span 6 chords		Drag Coefficient, k_D, for two dimensional flow		
	Lift Coefficient k_L	Drag Coefficient k_D	Experimental	Prandtl Theory	Ratio
6	0·040	0·0374	0·0343	0·0348	1·02
− 3	0·153	0·0246	0·0185	0·0181	0·98
0	0·268	0·0225	0·0137	0·0132	0·96
3	0·382	0·0284	0·0135	0·0130	0·96
6	0·494	0·0382	0·0153	0·0166	1·08
9	0·593	0·0508	0·0189	0·0203	1·07
12	0·682	0·0668	0·0252	0·0282	1·12

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* "The Prediction on the Prandtl Theory of the Lift and Drag for Infinite Span from measurements on Aerofoils of Finite Span" By A. Fage and H L. Nixon. 'R & M, No 903, Aeronautical Research Committee'

† Approximate values For full details of this calculation, see 'R & M., 903, *loc. cit*

that except near the critical angle the prediction on the Prandtl theory of the drag for two-dimensional flow is quite reliable Although the present paper is only concerned with drag it is of interest to mention that the lift for two dimensional flow can also be estimated with fairly satisfactory accuracy from force measurements on a rectangular aerofoil of finite span *

The Velocity and Pressure Diagrams

(11) Some interesting features of the wake are illustrated in fig 7 where curves of velocity and of pressure are given for the section 0 68 chord behind

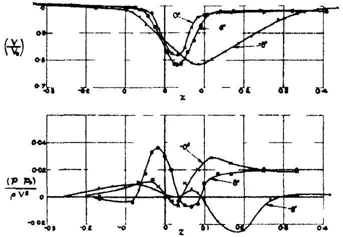

FIG 7 —Velocity and Pressure in the Section of the Wake 0 68 Chord behind Trailing Edge

the trailing edge The values of the pressure were not measured directly but have been estimated from the measurements of total head and of velocity The diagrams of velocity resemble in shape those of total head and indicate a pronounced drop of velocity at the centre of the wake The minimum velocity does not change appreciably as the incidence increases from −8° to +8° and has an average value of about 80 per cent of the undisturbed velocity The pressure diagrams show that there is no systematic variation of pressure across the wake and also that the average value does not differ appreciably from that in the surrounding stream It would appear therefore that at this distance behind the aerofoil nearly all the total head losses arise from the slowing up of the wake

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* *Cf* R and M 903

The sketches given in fig 8 show for the incidences −8° and +8° the opening out of the wake as it flows downstream It was estimated from a few tentative observations taken just forward of the trailing edge that at +8° incidence nearly all the total head losses in the wake were associated with the flow over the upper surface At 8 incidence the reverse was the case and the losses in the stream coming off the upper surface were only a very small fraction of the total

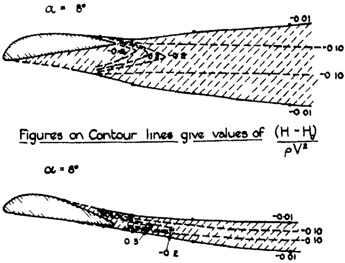
α = 8°
−0 01
−0 10
−0 10
−0 01
−0 2
Figures on Contour lines give values of $\frac{(H-H_0)}{\rho V^2}$
α = 8°
−0 01
−0 10
−0 10
−0 01
0 5
−0 2

Fig 8—Wake Diagrams

(12) In conclusion the writers wish to acknowledge their indebtedness to Dr H Lamb F R S for valuable suggestions made in regard to the arrangement of the paper

The Loss of Energy in Metal Plates of Finite Thickness, due to Eddy Currents Produced by Alternating Magnetic Fields

By Prof E W Marchant, D Sc, and J L Miller, B Eng

(Communicated by Sir E Rutherford,—Received April 20, 1926)

Introduction

The induction of eddy currents in metal plates which are subjected to alternating magnetic fields has been discussed by Clerk-Maxwell,* J J Thomson† and many others When an alternating magnetic field is produced normal to the surface of a metal plate, eddy currents are induced at the surface of the plate, which gradually penetrate its interior, the current dying away as it penetrates more deeply into the metal

The diffusion of the currents into the plate depends upon the self-induction and resistance of the paths along which they flow, and can be calculated by the same kind of formula as is used for determining the conduction of heat through a metal slab

When examining the energy loss due to eddy currents in metal plates of varying thicknesses, it was noticed that the total loss of energy due to these currents was, in some cases greater in thin plates than it was in thicker plates

In order to observe whether the phenomenon was affected by varying flux distribution across the plate, coils of different shape were constructed, giving magnetic fields of different form A somewhat similar phenomenon has been observed by J J Thomson† with high-frequency currents He showed that if a high-frequency current was passed round two coils and the strength of the current observed by the glow produced in an electrodeless bulb placed inside one of them, that a core of solid copper placed in the other did not appreciably reduce the glow in the bulb, whereas a piece of glass tubing of the same size coated with Dutch metal or with a film of silver deposited on it checked the discharge considerably He has shown that there is a certain thickness for which the heat produced is a maximum

Apparatus Used

In these experiments the energy loss in the metal plate was measured by determining the increase in effective resistance of an inductive coil (called the exploring coil) when brought near to the plate The arrangement of the circuit used is shown in fig 1 The proportional arms CB, CA of the Wheatstone

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* 'Electricity and Magnetism,' vol 2, p 396

† 'Recent Researches in Electricity and Magnetism,' p 323

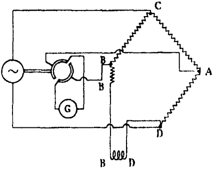

Fig 1

Bridge were non inductive resistances of "Eureka" wire and the third arm coil DA was a coil exactly similar to the exploring coil BD both in resistance and inductance Both coils were made of constant resistance "Eureka" wire wound on wooden bobbins

The bridge was supplied with constant frequency 50 cycle alternating current at constant voltage by means of a four pole alternator connected across CD

A galvanometer is connected between A and B the connection between it and the bridge being made through a two part commutator driven synchronously by an extension of the shaft of the alternator

The commutator consisted of two semi-circular copper discs mounted on an ebonite cylinder which was fixed to the alternator shaft The brushes were of the roller type and were made of thin flexible copper discs The use of this commutator and brush gear greatly reduced thermo electric effects and contact resistance variations

By rocking the brush gear round the commutator a position can be found where the rectified current is in phase with the impressed voltage when in this position and with nearly equal resistances in all the bridge arms it can be shown that the galvanometer current is given by

$$i_g = \frac{E R_1 \delta R}{R_g (R_1 + R_3)^2}$$

where

E is the pressure applied to the bridge in volts

- R_1 is the resistance of each of the proportional (non inductive) arms of the bridge
- R_3 is the resistance of the exploring coil and is equal to R_4
- R_g is the resistance of the galvanometer circuit
- δR is the change in effective resistance of the exploring coil

With the brushes in this position there is no appreciable galvanometer deflection if the inductance of one of the bridge arms is altered

To determine the change in effective resistance R of the exploring coil corresponding with the current flowing through the galvanometer experimentally a resistance of known magnitude was inserted in series with the exploring coil This resistance could be switched out of circuit by short circuiting it with a metal strap across two mercury contacts The current flowing through the galvanometer when the resistance was inserted agreed within limits of experimental error with that determined by the formula given above

Experimental Results

A large number of experimental results have been obtained with different coils some of which are shown in Table I Curves showing the change in effective resistance of coil A when placed 0.24 cm away from plates of different thicknesses are shown in fig 2

Table I

Coil	Fig	Mean diameter of coil in cm	Distance of coil from plate surface in cm	R for Cu R for Zn for thick plates	Max R R for thick plates (Cu)
A	Fig 2	4.45	0.24	1.3	1.3
	Fig 3	4.45	1.54	0.98	1.6
B		5.6	0.318	1.43	1.2
		5.6	0.56	1.27	1.5
C		5.7	0.470	1.2	
		5.7	0.792	1.08	1.4
D		12.2	0.238	0.93	1.6

It will be noticed that there is maximum resistance change when the copper plate is 0.5 cm thick

A similar curve is given for zinc plates, but the maximum is not so marked and occurs with a plate about 1 cm thick

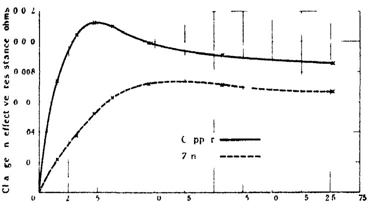

Fig 2 Change in Effective Resistance of Coil A Distance of Coil from Plates 0·24 cm

In fig 3 are shown similar curves for the same coil placed 1·54 cms away from the plate. Although the maximum change in effective resistance occurs

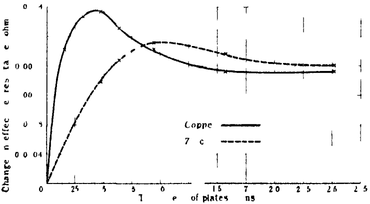

Fig 3 Change in Effective Resistance of Coil A Distance of Coil from Plates 1·54 cms

with a copper plate 0·5 cm thick and with a zinc plate about 1 cm thick the curves cross showing that with plates of about 1 cm thickness the energy loss with the lower conductivity plates is greater than with plates of greater conductivity. Particulars of the coils used in these experiments are given in Table II

Table II

Coil	Mean diameter cm	Number of layers	Resistance ohms	Inductance in 10^{-6} henry
A	4·45	10	10	440
B	5·6	1	0·09	4
C	5·7	2	1·45	11
D	12·25	2	11	35

The shape of the flux curves for coils A and B are given in fig 4 The curve for coil B has been plotted by means of a new integral found by Prof Proudman * which gives the value of the field at any point

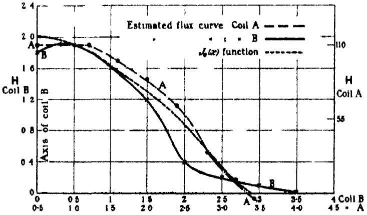

FIG 4 Magnetic Field due to Coil B obtained from $\int_0^\infty \lambda J_1(\lambda) e^{-\frac{\lambda z}{a}} J_0\left(\frac{\lambda r}{a}\right) d\lambda$

These results were verified by means of an estimation of the shape of the flux curve made from fig 18 vol 2, in Clerk Maxwell's "Electricity and Magnetism" for the field due to a single turn A similar curve is shown for coil A and it will be seen that these curves correspond roughly with the Bessel function distribution assumed in the theory

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* See Appendix p 614

MATHEMATICAL THEORY

General Equations

Using cylindrical polar co ordinates r θ z, let the corresponding components of electric and magnetic force be X Y Z and α β γ respectively Then the fundamental electromagnetic equations for the metal are

$$\left.\begin{array}{ll} \dfrac{4\pi}{\sigma}\mathrm{X} = \dfrac{1}{r}\dfrac{\partial\gamma}{\partial\theta} - \dfrac{\partial\beta}{\partial z} & \mu\dfrac{\partial\alpha}{\partial t} = \dfrac{1}{r}\dfrac{\partial \mathrm{Z}}{\partial\theta} - \dfrac{\partial\mathrm{Y}}{\partial z} \\ \dfrac{4\pi}{\sigma}\mathrm{Y} = \dfrac{\partial\alpha}{\partial z} - \dfrac{\partial\gamma}{\partial r} & \mu\dfrac{\partial\beta}{\partial t} = \dfrac{\partial\mathrm{X}}{\partial z} - \dfrac{\partial\mathrm{Z}}{\partial r} \\ \dfrac{4\pi}{\sigma}\mathrm{Z} = \dfrac{1}{r}\dfrac{\partial}{\partial r}(r\beta) - \dfrac{1}{r}\dfrac{\partial\alpha}{\partial\theta} & \mu\dfrac{\partial\gamma}{\partial t} = \dfrac{1}{r}\dfrac{\partial}{\partial r}(r\mathrm{Y}) - \dfrac{1}{r}\dfrac{\partial\mathrm{X}}{\partial\theta} \end{array}\right\} \quad (1)$$

while for the air $4\pi/\sigma$ is to be replaced by $\mathrm{K}\partial/\partial t$ In these equations σ is the specific resistance of the metal K the specific inductive capacity of the air μ the magnetic permeability and t is the time

Suppose that the field is symmetrical about the z axis so that $\partial/\partial\theta = 0$ and also that the magnetic force lies in planes through the z axis so that $\beta = 0$ Complex periodic vectors will be used in which the time only enters through the factor $\epsilon^{i\omega t}$ and only the real parts are to be interpreted Then for the metal equation (1) gives

$$\left.\begin{array}{ll} \mathrm{X} = 0 & i\omega\mu\alpha = -\dfrac{\partial\mathrm{Y}}{\partial z} \\ \dfrac{4\pi}{\sigma}\mathrm{Y} = \dfrac{\partial\alpha}{\partial z} - \dfrac{\partial\gamma}{\partial r} & 0 = 0 \\ \mathrm{Z} = 0 & i\omega\mu\gamma = \dfrac{1}{r}\dfrac{\partial}{\partial r}(r\mathrm{Y}) \end{array}\right\} \quad (2)$$

while for the air $4\pi/\sigma$ is to be replaced by $i\omega\mathrm{K}$ Eliminating γ α from (2) the following is obtained—

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\gamma}{\partial r}\right) + \frac{\partial^2\gamma}{\partial z^2} - \frac{4\pi i\omega\mu}{\sigma}\gamma = 0 \quad (3)$$

a solution of which is

$$\gamma = \mathrm{J}_0(\kappa r)\,\epsilon^{i\omega t}\{\mathrm{A}\epsilon^{z\sqrt{\kappa^2+4\pi i\omega\mu/\sigma}} + \mathrm{B}\epsilon^{-z\sqrt{\kappa^2+4\pi i\omega\mu/\sigma}}\} \quad (4)$$

for all values of the constants κ A B $\mathrm{J}_0(\ )$ denoting the Bessel's function of zero order

The corresponding expression for the air is

$$\gamma = \mathrm{J}_0(\kappa r)\,\epsilon^{i\omega t}\{\mathrm{A}\epsilon^{z\sqrt{(\kappa^2-\omega^2\mathrm{K}\mu)}} + \mathrm{B}\epsilon^{-z\sqrt{\kappa^2-\omega^2\mathrm{K}\mu}}\} \quad (5)$$

Now for such values of z and ω as we are to consider $z\omega\sqrt{(K\mu)}$ may be neglected so that wave effects in the air need not be considered

Undisturbed Field Due to the Coil

Suppose that there is a single turn of wire in the form of a circle of radius a in the plane $z = 0$ and carrying a current $u\epsilon^{i\omega t}$ Then on the axis of the coil * where $r = 0$

$$\gamma = 2\pi u\epsilon^{i\omega t}\frac{a^2}{(a^2+z^2)^{3/2}} \tag{6}$$

$$= 2\pi u\epsilon^{i\omega t}\int_0^\infty \epsilon^{-\kappa z}\kappa a J_1(\kappa a)\,d\kappa \tag{7}$$

for $z > 0$ where J_1 denotes the Bessel's function of the first order It then follows from (5) that both on and off the axis

$$\gamma = 2\pi u\epsilon^{i\omega t}\int_0^\infty \kappa a J_1(\kappa a)\,\epsilon^{-\kappa z}J_0(\kappa r)\,d\kappa \tag{8}$$

For a particular value of z the most important value of κ is that which makes $\kappa J_1(\kappa a)\,\epsilon^{-\kappa z}$ a maximum Now this occurs when

$$J_0(\kappa a) = \frac{z}{a}J_1(\kappa a) \tag{9}$$

and it will be seen that for small values of z the most important value of κ is about 2·4/a while for $z = a$ the most important value of κ is about 1·4/a

In the following one particular value of κ will be used though integral formulæ for general results can be deduced immediately

Field as Disturbed by Plates

Suppose the plane of the coil is given by $z = -d$ and that in the absence of the plate the field would be given by

$$\gamma = H\epsilon^{i\omega t - \kappa z}J_0(\kappa r) \tag{10}$$

for $z > -d$ H being a constant

Let the faces of the plate be given by $Z = 0$, $Z = -h$ and the disturbed field by

$$\gamma = J_0(\kappa r)\,\epsilon^{i\omega t}\{H\epsilon^{-\kappa z} + H'\epsilon^{\kappa z}\} \tag{11}$$

for $-d \leqslant z \leqslant 0$

$$\gamma = J_0(\kappa r)\,\epsilon^{i\omega t}\{A\epsilon^{-\kappa z\sqrt{(1+k)}} + A'\epsilon^{\kappa z\sqrt{(1+k)}}\} \tag{12}$$

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* See Appendix

for $0 \leqslant z < h$,

where

$$k = \frac{4\pi\omega\mu}{\kappa^2\sigma} \tag{13}$$

$$= J_0(\kappa r)\,\varepsilon^{\iota\omega t}\,C\varepsilon^{-\kappa z} \tag{14}$$

for $z \geqslant h$ H′ A A C being constants

At both faces of the plate, γ and $\partial\gamma/\partial z$ must be continuous so that

$$\left.\begin{array}{l} H \quad H \quad A + A \\ H \quad H = \sqrt{(1 + \iota k)}\,(A \quad A) \end{array}\right\} \tag{15}$$

$$\left.\begin{array}{r} A\varepsilon^{-\kappa h\sqrt{1+\iota k)}} + A\varepsilon^{\kappa h\sqrt{(1+\iota k)}} = C\varepsilon^{\kappa} \\ \sqrt{(1 + \iota k)}\,\{A\varepsilon^{\kappa h\sqrt{1+\iota k)}} \quad A\varepsilon^{\kappa h\sqrt{1 \quad \iota k)}}\} = C\varepsilon^{\kappa h} \end{array}\right\} \tag{16}$$

and from these the following is deduced

$$\frac{H'}{H} = \frac{-\iota k \sinh \kappa h\sqrt{(1 + \iota k)}}{(2 + \iota k)\sinh \kappa h\sqrt{(1 + \iota k)} + 2\sqrt{(1 + \iota k)}\cosh \kappa h\sqrt{(1 + \iota k)}} \tag{17}$$

In the plane of the coil the effect of the plate is to multiply the magnetic flux by

$$\frac{H\varepsilon^{\kappa l} + H\varepsilon^{\kappa l}}{H\varepsilon^{\kappa l}} = 1 + \frac{H}{H}\varepsilon^{2\kappa d} \tag{18}$$

Effective Resistance

Let the resistance and self inductance of the coil be R and L respectively so that the current u corresponding to an e m f $E\varepsilon^{\iota\omega t}$ is given by

$$(R + \iota\omega L)\,u = E\varepsilon^{\iota\omega t} \tag{19}$$

in the absence of the plate To allow for the presence of the plate the equation must be replaced by

$$\left\{R + \iota\omega\left(1 + \frac{H}{H}\varepsilon^{2\kappa d}\right)L\right\}u = E\varepsilon^{\iota\omega t} \tag{20}$$

or

$$\{(R + R) + \iota\omega(L + L)\}\,u = E\varepsilon^{\iota\omega t} \tag{21}$$

if

$$\frac{H'}{H}\varepsilon^{2\kappa d} = \frac{L'}{L} + \frac{R}{\iota\omega L} \tag{22}$$

where R′ and L′ are real R′ and L are the changes in the effective resistance and self-inductance of the coil.

Now take

$$(\lambda + i\nu) - 2\sqrt{(1 + ik)}$$

where λ, ν are real, so that

$$\tfrac{1}{2}\lambda^2 = \sqrt{(1 + k^2)} + 1, \qquad \tfrac{1}{2}\nu^2 = \sqrt{(1 + k^2)} - 1$$

From (17) and (22) it can be shown that

$$\frac{\mathrm{R}'}{\mathrm{L}\omega}\epsilon^{2\kappa d} = \frac{k}{\mathrm{D}}\{2\cosh\lambda\kappa h + \lambda\sinh\lambda\kappa h - 2\cos\nu\kappa h + \nu\sin\nu\kappa h\} \tag{23}$$

where

$$\mathrm{D} = \lambda^2(1 + \tfrac{1}{4}\lambda^2)\cosh\lambda\kappa h + \lambda^3\sinh\lambda\kappa h$$
$$+ \nu^2(1 - \tfrac{1}{4}\nu^2)\cos\nu\kappa h - \nu^3\sin\nu\kappa h \tag{24}$$

It will be seen that (23) is a function of k and κh only

Thick Plates

On taking κh large, the principal part of (23) is

$$\frac{\mathrm{R}'}{\mathrm{L}\omega}\epsilon^{2\kappa d} = \frac{\lambda - 2}{k}, \tag{25}$$

which is a function of k only

For small values of k the function (25) takes the form of $\tfrac{1}{2}k$, while for large values of k it becomes

$$\sqrt{2/k} \tag{26}$$

The function $(\lambda - 2)/k$ reaches a maximum value of 0·3 when $k = 4·115$, and this fact elucidates the difference between figs 2 and 3

Variations with Thickness of Plate

Taking first the limiting case when $k = 0$, from (23) it follows

$$\frac{\mathrm{R}'}{\mathrm{L}\omega}\epsilon^{2\kappa d} = \tfrac{1}{2}k\{1 - \epsilon^{-2\kappa h}\}$$

and R′ steadily increases with κh towards its limiting value. Taking next the limiting case when $k \rightarrow \infty$, from (23)

$$\frac{\mathrm{R}'}{\mathrm{L}\omega}\epsilon^{2\kappa d} = \sqrt{\left(\frac{2}{k}\right)}\frac{\sinh\kappa h\sqrt{2k} + \sin\kappa h\sqrt{2k}}{\cosh\kappa h\sqrt{2k} - \cos\kappa h\sqrt{2k}}, \tag{27}$$

except when $\kappa h\sqrt{(2k)}$ is very small, when (27) must be replaced by

$$\frac{1}{\tfrac{1}{2}k\kappa h + \dfrac{1}{k\kappa h}}.$$

This reaches a maximum value of 0.707 when $\kappa h = \sqrt{2}/k$. Thus it will be noticed that the change in effective resistance for plates of increasing thickness rapidly reaches a maximum and then decreases towards the limiting value for thick plates. Also we see that the ratio of the maximum R′ to the limiting R is $\frac{1}{2}\sqrt{k}$.

Comparison with Experiments

In the experiments $\mu = 10^{-9}$ henry/cm. For copper $\sigma = 1.6 \times 10^{-6}$ ohm cm, $\omega = 100\pi$/sec, so that

$$\frac{4\pi\mu\omega}{\sigma} = 2.5\ \text{cm}^{-2}.$$

Assuming that σ for zinc is four times that for copper, it may be seen from (13) that for each κ, k for zinc will be a quarter that for copper.

From (25) the two values of k are found which give the ratio of column 5 of Table I, and these are given in Table III. The remaining columns of Table III are based on the equations (13) and (25).

Table III

Coil	k		κ cm^{-1}	$\epsilon^{-\kappa d}$	$\frac{R}{L\omega}$	
	Cu	Zn			Cu	Zn
A	5 9	1.25 2.25	0.7 0.53	0.715 0.142	0.22 0.142	0.154 0.147
B	4.5 5.5	1.1 1.4	0.75 0.68	0.62 0.467	0.186 0.14	0.13 0.108

It will be seen that the effective values of κ obtained are of the order of those indicated by equation (9), also that an increase in the distance of the coil from the plate reduces the value of κ as the theory indicates.

It is easy to see, however, that the calculated values of R/Lω will be too large. For on account of the factor $\epsilon^{-2\kappa d}$ in the formula for this quantity the range of important values of κ in L will be greater than that in R, but the use of an effective κ may be expected to agree with experiments as regards ratios of effects.

The mathematical theory given has been worked out by Prof. Proudman, F.R.S., to whom the authors are very greatly indebted for his interest in the experiments.

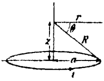
APPENDIX

Calculation of the Flux Curve due to the Single-layer Coil

The magnetic field due to a single turn, carrying a current i, at any point along its axis is given by

$$\gamma = \frac{2\pi i a}{R^2}\cos\theta = \frac{2\pi i a^2}{R^3} = 2\pi i\left[\frac{a^2}{(a^2+z^2)^{3/2}}\right]$$

where i is the C G S current through the coil



Now

$$\int_0^\infty \varepsilon^{-\kappa z} J_0(\kappa a)\,d\kappa = \frac{1}{(a^2+z^2)^{\frac{1}{2}}}$$

hence

$$\int_0^\infty \varepsilon^{-\kappa z}\,\kappa J_0'(\kappa a)\,d\kappa = -\frac{a}{(a^2+z^2)^{3/2}}$$

and

$$\gamma_{axis} = -2\pi i\int_0^\infty \varepsilon^{-\kappa z}\,\kappa a\,J_0'(\kappa a)\,d\kappa$$

It is shown on p 610 that the value of γ at any point $(r\,z)$

$$= -2\pi i\int_0^\infty \kappa a J_0'(\kappa a)\,\varepsilon^{-\kappa z} J_0(\kappa r)\,d\kappa$$

$$= 2\pi i\int_0^\infty \kappa a J_1(\kappa a)\,\varepsilon^{-\kappa z} J_0(\kappa r)\,d\kappa$$

If

$$\kappa a = \lambda$$

$$\gamma = \frac{2\pi i}{a}\int_0^\infty \lambda J_1(\lambda)\,\varepsilon^{-\frac{\lambda z}{a}} J_0\!\left(\frac{\lambda r}{a}\right)d\lambda$$

To get the shape of the flux curve due to a single turn at a given distance z, it is necessary to evaluate

$$\int_0^\infty \lambda J_1(\lambda)\,\varepsilon^{-\frac{\lambda z}{a}} J_0\!\left(\frac{\lambda r}{a}\right)d\lambda$$

for several values of r

To find the flux curve for a flat coil of 10 turns, the flux curve for four turns, the innermost, the third, the sixth and the outer turn was calculated, and by summing these curves, an approximate field form was determined See fig 4 (B).

On the Nature of Atmospherics—II.

By E V Appleton, M A, D Sc, R A Watson Watt, B Sc, F Inst P, and J F Herd, A M I E E

(Communicated by Sir Henry Jackson, F R S —Received April 23, 1926)

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I —*Introduction*

In a previous paper* we gave a preliminary account of an experimental method of determining the intensity and duration of those naturally occurring electric waves known as atmospherics The method consisted in examining, by means of a sensitive cathode ray oscillograph, the potential variations developed across a condenser or resistance included in a damped antenna, the time constant of which was small compared with the duration of the atmospheric pulse A summary of the chief characteristics of the first six hundred atmospherics investigated by this method was also given, but, as the work was obviously of a preliminary nature, the detailed discussion of the results was not considered profitable at such an early stage and was accordingly postponed Since that time the observations have been systematically continued, and many alterations and improvements have been made in the experimental apparatus which tend to make the oscillographic trace a still more faithful representation of the electric field changes In particular, the development and use of a new form of oscillograph time base, which is both linear and unidirectional, has eliminated the distortion and ambiguity as to time-sense which was associated with the use of the simple harmonic time base of the earlier experiments Also, as the apparatus for the delineation of atmospheric waveforms is now more or less in its final form, and as the circuit ultimately developed is somewhat complicated, a series of station tests has been devised which enable the observer rapidly to ascertain at any moment if the aerial and internal insulation is satisfactory and the required quality of amplification is being maintained

The oscillographic observations have been supplemented by simultaneous and independent determinations of the measurable semi-permanent changes of the earth's electric field which have been found to be associated with a small percentage of atmospherics It may be noted that the possibility of such net changes of field was purposely excluded from our first account of the method *

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* 'Roy Soc Proc.,' A, vol 103, p. 84 (1923).

The nature of the alterations and the supplementary observations mentioned above may perhaps best be understood when the problem is viewed from a standpoint differing slightly from that adopted in the first paper Following the procedure of wireless telegraphy we there regarded the action of an atmospheric on an antenna as the introduction of a transient electromotive force in the system, the initial and final values of the electromotive force being zero Such a simple assumption is undoubtedly valid for a great majority of atmospherics in Great Britain during the winter months We may, however, more generally regard an atmospheric as a rapid alteration of the earth's electric field, the final value of the field not necessarily being the same as the initial value This enables us to include the small but interesting class† of atmospherics mentioned above, the consideration of which was excluded from the earlier communication Such a method of viewing the problem is physically more transparent than is the usual procedure of wireless telegraphy, and leads more directly to a proper realization of the possibilities and limitations of the methods used

II —*Basis of Methods Used*

Let us consider the effect of a rapid variation of the earth's electric field on an exposed conductor, of concentrated capacity C_0, which is situated at a height h and earth-connected through a resistance R (see fig 1)

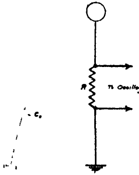

FIG 1

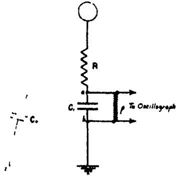

FIG 2

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* *Loc. cit.*, p 85, footnote.

† The original observations were made in the winter months of 1922–3 During the summer months of 1923 and 1924 the increased frequency of local thunderstorms has made this class correspondingly more important, and particular attention has been paid to it

Let us suppose that the system is non-oscillatory, and that the time constant C_0R is made so small that the charge on the exposed conductor follows, without appreciable lag, the electric field variation, in which case the potential of the conductor does not depart sensibly from its normal zero value Let the potential V at height h be $hf(t)$ where t is the time and $f(t)$ the electric field, and let the charge on the exposed conductor at any instant be Q We then have

$$\frac{Q}{C_0} + V = \frac{Q}{C_0} + hf(t) = 0 \tag{1}$$

Further, the potential v developed across the ends of the resistance R is given by

$$v = -R\frac{dQ}{dt} - RC_0\frac{dV}{dt} = hRC_0f'(t) \tag{2}$$

As it is possible to examine the transient potential changes across R by means of a cathode-ray oscillograph, as previously described, it is thus possible to investigate the rate of change of the earth's electric field It may further be noticed that this method is equally valid for atmospherics of local and of distant origin For atmospherics of distant origin the initial and final values of V are sensibly the same so that the resultant quantity of electricity passing through R is zero On the other hand, if the atmospheric is due to a near lightning flash there will be a measurable nett transport of electricity up or down the earth connection depending on the sign of the resultant change of field When the potential changes across the resistance R are examined, using the uniform time base to be described, the oscillographic trace gives us a record of the rate of change of the potential gradient $\left(i\,e\ \frac{1}{h}\ \frac{dV}{dt}\right)$ as a function of the time t It is obvious, from what has been said immediately above, that for atmospherics of distant origin the area* bounded by the trace will be zero, while for atmospherics due to near lightning flashes the area of the curve will not be zero, and will give us information regarding the sign and magnitude of the resultant transport of electricity through the resistance R and therefore of the net change of the earth s field.

Since the changes of the earth's field to be studied are relatively small, it is necessary to use an exposed conductor of large dimensions which it is impossible to insulate perfectly The ideal conductor for this purpose would be a large sphere or spherical cage raised by a shielded lead to a great height, but as the large capacity necessary for the detection of small field changes demands a radius of prohibitive size, a large aerial with a long horizontal portion has been used instead The capacity of the aerial was 2.77×10^{-9} farads, being thus equivalent to that of a sphere of over 23 metres radius The effective height of the aerial was 15 metres * When a resistance R of 2,000 ohms was used a deflection of 1 mm on the screen of the oscillograph, used without amplifier, corresponded to a rate of change of field of about 10^4 volts per metre per second When the linear voltage amplifier was used this sensitivity was increased 18 times with one stage of amplification, and 300 times with two stages

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* Allowing for the difference in sign between the areas above and below the axis of t.

If the potentials developed across a condenser inserted in the aerial (see fig 2) are examined, the resistance R being large enough to keep the circuit non-oscillatory, it is possible to investigate directly the variation of the field itself instead of the rate of change But a certain amount of caution is necessary in interpreting the results for cases in which the initial and final values of the field are not the same

The matter is complicated by the fact that the aerial insulation cannot be made perfect and that for the correct operation of the triode amplifier the resistance between points *a* and *b* (which are connected respectively to the grid and filament of the input triode of the amplifier) must not be too large The effect of imperfect insulation between the aerial and earth and between the plates of the condenser C is represented diagrammatically by the high resistance ρ in fig 2

Let us consider the effect on this system of a rapid change of the earth's electric field Before the change the exposed conductor retains a bound charge Q_0 consistent with the normal potential at a height *h*, the unbound charge leaking away and the system being at zero potential If V_0 is the normal potential at the height *h* then

$$V_0 + \frac{Q_0}{C_0} = 0 \tag{3}$$

Now let us suppose that the vertical electrical field undergoes a change of magnitude $f(t)$ The potential at a height *h* will be increased by $hf(t)$. This will bring about a separation of charge Q in the aerial system since the connection is metallic, and, if the time constant of the circuit is sufficiently small, the separation of charge will be proportional to the change of potential We may, as a first approximation, neglect the effect, during this change, of the resistance ρ.

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* Watt & Appleton, *loc. cit*, p 93

The expression of the fact that the potentials of C_0 and C are still identical is that

$$V_0 + hf(t) + \frac{Q_0}{C_0} - \frac{Q}{C_0} = \frac{Q}{C_1}, \tag{4}$$

or subtracting (3), that

$$hf(t) = \frac{Q}{C_1} + \frac{Q}{C_0}, \tag{5}$$

Let the potential across the plates of C_1 which is examined oscillographically, be v Then

$$v = \frac{Q}{C_1} \tag{6}$$

and

$$f(t) = \frac{v}{h}\,\frac{C_0 + C_1}{C_0} \tag{7}$$

We thus see that, by the use of what may be described as a condenser potentiometer, we may, by measuring v, determine a known fraction of the potential gradient changes But certain conditions must be fulfilled in order that the potential variation across C_1 should be representative of the field change In the first place, as previously mentioned, the system must be non-oscillatory and the time constant of the whole system must be small compared with the duration of the field change Secondly, the time constant $C_1\,\rho$ must be large compared with the duration of the field change The second condition is the one more difficult to maintain in practice, and a more detailed reference will be made to it later

Let us now consider the effect of an atmospheric disturbance involving a semi-permanent change of the field when the condenser method (see fig 2) is used It is seen that the resultant induced charge on the exposed conductor or aerial is different before and after the disturbance From (5) we may deduce that for a net increase of field strength [E] the charge is diminished by [Q], where

$$h[E] = \frac{C_0 + C_1}{C_1 C_0}[Q] \tag{8}$$

At the end of the disturbance this charge disappears by leakage through the resistance ρ and in a time determined by the time constant $(C_0 + C_1)\,\rho$ We thus see that an exponential oscillographic trace of long duration (*i e*, of the order of $5(C_0 + C_1)\,\rho$ seconds) is to be expected as the result of a net change of field. These traces are observed in actual practice and special mention of them will be made later We need only note here that if the maximum potential change indicated by the beginning of the exponential trace is v, the net change of the electric field [E] is given by

$$[E] = \frac{1}{h}\left(\frac{C_0 + C_1}{C_0}\right) v \tag{9}$$

Two other methods of measuring these small semi permanent changes of electric field have been used These methods have not involved the use of the oscillograph and consist in measuring the charge [Q] passing to earth as a result of the disturbance In each case equation (8) is applicable

As an example of the sensitivity of the assembly when used for the determination of the changes of the electric field, the case in which C_1/C_0 is unity may be taken as typical In this case, with one stage of amplification, a deflection of 1 mm on the oscillograph screen corresponds to a field change of 0 0074 volts per metre

III —*Details of Atmospheric Wave-form Apparatus*

As mentioned above, the exposed conductor used for measurements of E and dE/dt variations was an L aerial with a long horizontal portion of 500 metres and an effective height of 15 metres The capacity C_0 of this aerial was $2\ 77 \times 10^{-9}$ farads The maintenance of a high aerial insulation resistance was frequently a matter of difficulty, but was finally solved by the use of special sulphur-ringed insulators [*] These were in the form of rods of 1½-inch ebonite with two wide drying flanges. The leading-in insulator was in the form of a tall ebonite tube with three drying petticoats, the whole being further protected by a metal cone With these modifications the aerial insulation resistance was always maintained at a value high compared with the 10 megohms leak The insulation test is described later

The internal circuit consists of the amplifier, oscillograph, time base apparatus, switching systems and testing devices As the final assembly developed has become somewhat complicated, it will be most convenient to describe this briefly in sections

In fig. (3) are shown the essential connections of the aerial, amplifier and oscillograph with the incomplete connections to the linear time-base oscillator and testing devices

The resistance R[†] was such as to be just greater than that required for critical damping, as calculated for the value of the residual inductance in the circuit.

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[*] *Cf* C T R Wilson, 'Phil Trans. Roy Soc,' A, vol 221, p 75 (1920).

[†] The resistances R and R_1 were both anti inductively and anti-capacitatively wound

In this way the possibility of free oscillation was prevented and yet the response of the system to rapid changes made as faithful as possible The value of C_1/C_0 was usually a small integer

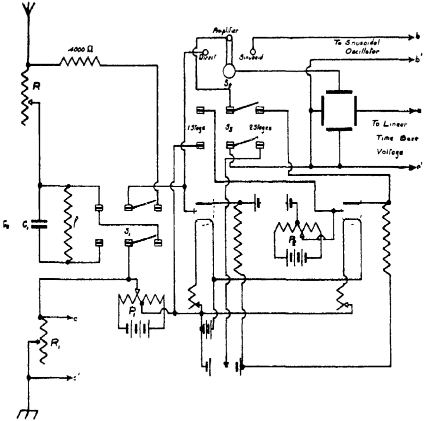
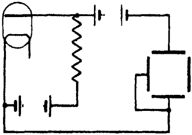


FIG 3

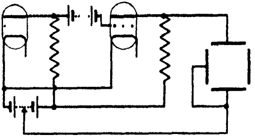
The Switch S_1 provides facilities for joining the amplifier input alternatively across the condenser C_1 (for measurement of E) or across the resistance R (for measurement of dE/dt) Since there was in the latter case a possibility of the formation of an oscillatory circuit by the aerial grid-filament capacity and earth, a damping resistance of 4 000 Ω was inserted in the grid lead

By means of the switch S_2 the potential developed across the condenser C_1 (E method), or the resistance R (dE/dt method), can be transferred with amplification (switch to "Amplifier") or without amplification (switch to "Direct") to the plates of the oscillograph producing vertical deflection These plates can also be disconnected from the observing system (switch to "Sinusoid") and connected to a sinusoidal oscillator for calibration of the time-base With the switch S_2 to "Amplifier" one or two stages of amplification can be introduced by means of the switch S_3

The skeleton amplifier connections in the two cases are shown in fig 4



(a) One Stage



(b) Two Stages

FIG 4

It will be seen that in the case of single stage amplification the connections are those of the conventional arrangement of resistance battery coupling, a battery of 170 volts being employed to neutralise the steady voltage drop across the 0·1 megohm resistance in the anode circuit of the triode With two stages, this battery is similarly used to neutralise this potential for application to the second grid, with fine adjustment on the potentiometer P_2 The amplifier battery is then tapped at a suitable place, as shown, to neutralise the voltage drop across the second anode, an economy of one neutralising battery being thereby effected With one stage of amplification the magnification was 18, while with two stages this was increased to 300. The oscillograph used was of the Western Electric Company type and worked very well. A tube specially made up by that company, with a screen of zinc silicate kindly supplied by Sir Herbert Jackson, was found to be much superior in response to transient deflections of short duration to the tubes supplied commercially. To increase the brilliance and duration of visible fluorescence on the oscillograph screen (on which depends the possibility of seeing atmospheric wave-forms and particularly of delineating the ripples which are often superposed on the main wave-form) the tubes were often over-run with anode potentials (500 volts) considerably higher than the normal value (350-400 volts). In such cases, since focussing could not be effected satisfactorily by the adjustment of filament current as usual a coil was arranged with its axis coincident with the electron beam. By adjusting a steady current through the coil and its position with respect to the tube, magnetic "focussing" was utilised. The distortion of the screen image due to the helical path of the electrons in the axial magnetic field was negligibly slight.

As mentioned in section II the maintenance of a high time-constant for the C_1 ρ circuit is essential, both for the portrayal of ordinary atmospherics and for the recognition of net field changes. The maintenance of this condition has been facilitated by the use of Western Electric Company triodes (type 102 D W) which have been used throughout for amplification purposes. When the caps of these tubes are removed it is possible to maintain a grid impedance of the order of 40 to 50 megohms, so that, since the inserted parallel resistance across C_1 is 10 megohms, the value of ρ is 8 megohms. The value of the time constant $(C_0 + C_1)\ \rho$* has thus not been less than 20,000 micro-seconds. The effect of a net change of field is then to produce across C_1 an exponential fall of potential which falls to 1/100 of its initial value in about 1/10 second. Such a potential change produces an oscillographic trace with a duration equal to that of a large number of sweeps of the indicating spot, and is thus easily recognised.

It is noteworthy that the interposition of one stage of amplification is also very important in removing from the terminals of the condenser C_1 the shunting effect of the relatively low resistance oscillograph thus maintaining a higher value of time constant.

We now turn to the parts of the circuit which for convenience have been omitted from fig. 3.

In the earlier experiments on the delineation of wave-form a simple harmonic time base of frequency 100-15,000 per second was used. This was obtained by connecting to the plates of the oscillograph producing horizontal deflections the terminals of a coil electro magnetically coupled to the circuit of an oscillating triode Although the oscillographic trace of an atmospheric obtained with such a base could be corrected for the distortion due to the non-uniform motion of the indicating spot, the rather serious ambiguity as to the correct time-sense still remained Thus it was not possible (except by using magnetic leakage to open the base to a narrow ellipse in which the sense of rotation was determinate) to decide whether to interpret the oscillographic trace indicating the sequence of electric field changes from left to right or *vice versa* Both of these difficulties and inconveniences have been satisfactorily removed by the development of a special type of triode oscillator* such that, when the potential changes from it are applied to the oscillograph plates, the cathode-ray spot moves uniformly from left to right over a suitable range in a definite and controllable time, returning to zero almost instantaneously Using such a time base there is no ambiguity as to the sequence of events in the atmospheric, since only the left to right transit of the spot is visible The circuit used for supplying the required voltage changes is shown in fig 5, where the connections (*aa'*) with the main circuit (see fig 3) are also depicted

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* The method of testing this time constant is described below.

The inductances L_1 and L_2 consist of two flat spiral coils coupled in such a way as to cause the triode circuit to generate oscillations of high frequency No additional capacities are connected across these coils, but the natural capacities complete the oscillating circuits which have a frequency of about one million cycles per second In the grid circuit of this oscillator is connected the condenser C in parallel with a triode of the dull emitter type (Marconi-Osram) used as a diode With suitable adjustments of currents and applied potentials such an oscillator can be made to generate very brief trains of oscillations alternately with uniform periods of quiescence †

During the short train of oscillations the grid side of the condenser C is rapidly charged up negatively so that the cathode ray spot in effect travels almost instantaneously from right to left The oscillations then cease, and the condenser C is discharged at a uniform rate through the saturated diode D, in a time determined by the constants of C and D, causing the spot to travel uniformly from left to-right during the quiescent period of the oscillator The short train of oscillations then begins again and the whole process is repeated

To make the right to left journey of the spot exceedingly rapid the natural frequency of the oscillatory circuits is kept high and the capacity of condenser C kept as low as possible (*e g* , less than 0 01 μ F) The control of the rate of uniform discharge of the condenser is most conveniently effected by controlling the filament current of the diode D The maximum voltage acquired by the grid side of the condenser C, and thus the amplitude of the movement of the cathode ray spot, is most easily controlled by regulating the filament current and the anode potential of the triode Potential changes of 8 to 15 volts corresponding to amplitudes of 8 to 15 mm time-base are commonly used

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* British Patent, No 235254 (Application dated 11th February, 1924)

† A more detailed account of this oscillator, which is an interesting example of a non-linear vibrator, is given in Appendix 1 to the paper " On the Nature of Atmospherics—III "

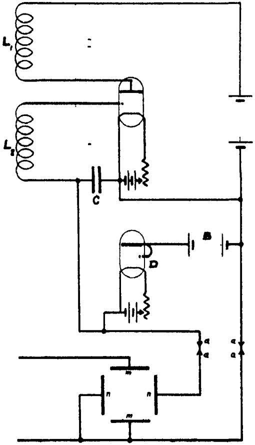

Fig. 5

The linearity of the time-base is fairly obvious from the uniformity of the intensity of the trace in the absence of atmospherics, but a more satisfactory check is obtained by causing the trace to move rapidly across the screen in a vertical direction by deflecting the electron beam with a moving magnet. A series of parallel straight lines with no trace of " backstroke " is obtained.

With the arrangement described it was found that the linearity of the left-to-right movement of the cathode-ray spot could be improved by the insertion of an anode battery, as at B, in order completely to saturate the diode. As this battery acts effectively in series with the resistance of the oscillograph between the plates *nn'* (of the order of 2 megohms) it should be of considerable voltage, *e.g.*, 75 to 100 volts. The instrument now in use gives practically complete linearity over the whole of its working range.

The frequency of the condenser discharges, and therefore the time of transit of the cathode ray spot along the base line is in practice best determined by applying, via the connection *b b'* (see fig. 3 with switch to " Sinusoid ") a simple harmonic voltage of known frequency to the plates *m m'*, producing vertical displacement of the electronic beam. With simple frequency relations between the two voltages a stationary pattern is obtained, from which the frequency of the condenser discharges may very easily be deduced.

In addition to providing a rapid means of frequency adjustment and calibration, this test readily reveals the achievement of the optimum conditions of linearity and of short duration of the return stroke. This latter condition is usually found when the oscillator filament is at its maximum working brightness.

Certain difficulties of observation occur in practice. These arise from the very unusual type of aerial circuit as judged from a radiotelegraphic point of view. The aerial, being necessarily aperiodic, is liable to signal interference from near-by transmitting stations. The high resistance, however, permits very little interference from the various British and Continental highly powered stations, none of which is very near the observing station, and the only interference experienced has been of quite local origin.

Trouble has also been experienced, both at Aldershot and in the course of similar observations at a station in Egypt, due to leakage current from alternating mains entering the aerial system from the earth, and giving rise to quite sensible voltages across C_1.

It may not be superfluous to add that frequent observations were made with a telephone interposed in the anode circuit of the amplifier, and that no image ever appeared on the screen during these tests without a corresponding sound being heard in the telephones. Moreover, simultaneous observations on the oscillograph circuit and on a normal radiotelegraphic receiver showed complete agreement between the incidence of images on the oscillographic screen and sounds in the telephones of the receiver

IV —*Testing Arrangements*

The arrangement of the test circuit is shown in fig 6 This apparatus is arranged to give two distinct types of impulse in the aerial circuit With the double pole two-way switch to the right-hand position, the condenser of 0 33 μ F is, by movement of the tapping key shown, charged and discharged through a coil of 0 1 Henry, a resistance R_2 (variable up to 2,000 Ω) and the small resistance R_1 in the aerial circuit (variable up to 200 Ω) By this means a short transient electromotive force, from an oscillation of moderate damping down to a highly damped and completely aperiodic impulse, can be introduced into the aerial circuit via the small coupling resistance R_1. It is thus possible to simulate the shape, voltage and duration of many of the observed radiation types of atmospherics described and illustrated later in this paper The comparison of the screen image with that calculated from the constants of the test impulse thus provided a means of testing if all circuits were in working condition For purposes of actual observation, the resistance R_1 was reduced to zero, and the test apparatus disconnected from it.

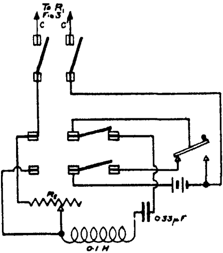

FIG 6

With the switch to the left-hand position, facilities are available for the reproduction, in the aerial circuit, of the conditions experienced when an impulse of the net change type is received For this purpose R_1 should have an infinite or very high value, so that, when the tapping key is open, the steady voltage of the test circuit battery is applied in the aerial circuit Closing the key short circuits the battery from the aerial circuit (the battery being protected by the guard resistance R_2), thus giving an aerial discharge of the net change type already discussed This test not only proves very useful in demonstrating the fidelity of the circuits for the delineation of this type of discharge, but, in addition, is a very convenient routine test of insulation, more particularly of the less controllable insulation resistance of the aerial circuit On account of the steady current flowing up or down the aerial due to natural causes, it is frequently impossible or unreliable to measure its insulation by any of the usual methods of direct current test, while any fall in the value of this resistance has the effect of an additional leakage path across the condenser C_1, with a consequent reduction of the time constant $(C_0 + C_1)\,\rho$

The test circuit has also been applied in a similar manner to another external aerial having mutual electrostatic capacity with the aerial system used for these observations Employed for the generation of impulses of the net change type, this gave a very rigorous reproduction of the natural conditions existing with this type of field change, and proved the accuracy of the observing apparatus in revealing such discharges of both electrical signs Used for the simulation of radiation field changes of varying amplitude, it was also effective in revealing the fidelity with which the observing system responded, within the known limits of the amplifier This was particularly useful in showing that a transient voltage, making the grid positive with respect to the filament by an amount exceeding the threshold value* (3 5 volts above normal) at which grid current commenced, produced cumulative rectification in the grid circuit and gave rise to a spurious impulse liable to be mistaken for a field of the net change type

In addition to these tests, direct current measuring instruments (not shown in fig 3) can be inserted at various places to verify the maintenance of standard amplifier conditions

Another useful test is the verification of the numerical value of amplification and the absence of distortion in amplitude or phase at all frequencies within the limits of comparability with the atmospherics to be observed

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* We have more recently found it desirable to increase this threshold value very considerably by using a triode with a very low amplification factor (L S. 5A) in the preliminary stage of the amplifier

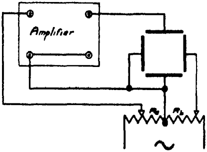


Fig 7

This was done by the arrangement shown in fig 7

An oscillator (of from 50 to 10,000 cycles) is connected to a resistance box of very low time constant tapped in two variable sections, one joined directly to the oscillograph plates producing horizontal deflection, and the other, through the amplifier, the output of which is to be measured, to the plates producing vertical deflection The resistances are then adjusted until the resultant line is tilted at 45° to either axis, whence it is known that the two pairs of plates are each being activated by co-phasal harmonic voltages of equal value It then follows that the amplification due to the triode stage is given directly by the ratio R_b/R_a This arrangement has the advantage of being independent of variation of oscillator output with frequency, since such variation affects each component equally

Tested in this manner over a range of 50 to 10,000 cycles, the single-stage amplifier, used for all quantitative measurements in these observations, has been shown to have a net amplification over this range equal to that at zero frequency, with an entire absence of measurable phase distortion

The complete agreement between the amplification at zero and at high audible frequencies permits a simple scale to be marked on the tube screen, relating the amplifier input voltage (*e g*, from the potentiometer P_1 of fig 3) to the screen deflection The accuracy of this calibration and the constancy of amplification ratio are thus simply and rapidly tested

From the satisfactory results of the tests described above made on artificial atmospherics, it is fairly certain that electric field changes are faithfully represented on the oscillograph screen with the normal working circuit. It is, however, of interest to note here the results of some comparative tests made with the normal circuit and with another circuit which should give complete fidelity. Let us consider an oscillatory circuit as illustrated in fig 8, where L_0 and kL_0

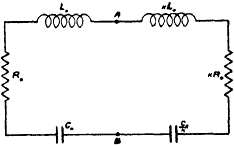


Fig 8.

are inductances, R_0 and kR_0 are resistances and C_0 and C_0/k are capacities, k being a constant Suppose a variable electromotive force $\phi(t)$ is introduced in the coil L_0 Then, if Q is the charge on either condenser, we have

$$(1+k)\left(L_0\frac{d^2Q}{dt^2}+R_0\frac{dQ}{dt}+\frac{Q}{C_0}\right)=\phi(t) \tag{10}$$

Suppose now that we are able to examine oscillographically the potential v between the points A and B In this case we have

$$v=k\left(L_0\frac{d^2Q}{dt^2}+R_0\frac{dQ}{dt}+\frac{Q_0}{C}\right)=\frac{k}{1+k}\phi(t) \tag{11}$$

In other words with a suitably balanced circuit, the *free* circulation of electricity (oscillatory or exponential), resulting from any impulse, produces no potential difference between the two points A and B, so that the temporal variation of the impressed electromotive force is registered with complete fidelity. It is convenient to take k as unity, so that in such a case

$$v=\frac{\phi(t)}{2} \tag{12}$$

Applying this result to our problem it is clear that C_0, R_0 and L_0 may represent the outside effective aerial capacity, resistance and inductance respectively, while kL_0, kR_0 and C_0/k may represent the similar quantities completing the aerial circuit in the indoor assembly The oscillograph may be connected via the grid circuit of the amplifier to points A and B.

Many comparative tests were made using this circuit and also the normal working circuit (which corresponds to a case in which kL_0 and kR_0 are zero), and no difference could be detected in the types of atmospheric impulses delineated in the two cases

In relation to the general accuracy of the measurement of duration by delineating the electric force E on the oscillograph screen, it should be remarked that frequent observations in which dE/dt and not E was delineated, though not yielding many detailed drawings of form, gave close agreement with the normal method in the mean durations of disturbances

V —*Programme of Observations*

1 *Period of Observations* —The preliminary results reported in the previous paper were obtained during the period November 22nd, 1922, to February 12th, 1923, and principally between January 27th and February 12th, 1923, when 590 wave forms were delineated The results now to be discussed fall into four groups, the first being that of the first paper, the second containing 1,200 observations on sinusoidal bases during the period February 14th to March 29th, 1923, the third containing the first group of observations, 749 in number, obtained with the linear time base, between April 20th and June 14th, 1923 In June and July, 1923, special attention was given to work with the capillary electrometer, while the fourth and main group of oscillographic observations, 5,813 in number, covers the period August 22nd to November 13th, 1923

In view of the facts that the observations in the fourth period so greatly outnumber those in the earlier periods, that they have the advantages of discrimination provided by the linear time base, and that they were taken by a single observer under relatively constant conditions and with a fixed programme, the detailed discussion of results will be concerned almost exclusively with this group, the smaller and earlier groups being utilised for comparison only, save in the extraction of grand means for peak field strength and duration

2 *Programme of 4th Series* —In the fourth series of observations, the work was done to a systematic time-table, at fixed hours, equal quarter-hour periods being allotted to observations on five standard time bases, in order to give equal weighting to all durations It need hardly be pointed out that the nature of the images obtained on the oscillograph screen renders it impossible to delineate forms departing greatly in duration from the base period in use at the moment, so that a wide range of base periods must be employed if fair sampling is to be attained. The time of observation was from 2,000 to 2,115 G M T, divided into quarter hours allotted respectively to bases of 11,760, 7,820, 3,910, 1,950, and 1,000 microseconds. The standards of time were a series of tuning forks of

corresponding frequency (85, 128, 256, 512 and 1,000 cycles per second), the note given by the linear oscillator being at first, compared aurally with that of the appropriate fork, while, later, comparison was made oscillographically with the output of an audio-frequency sinusoid oscillator calibrated against the forks

It must be admitted that this adoption of a mainly harmonic series of bases, convenient as it is from an operational standpoint, was unfortunate, since, in combination with the inevitable selection of forms of duration comparable with the base in use at the moment, it introduces a spurious periodicity into the observed durations, which renders unfruitful any attempt to detect true periodicities, which would be of very great interest in relation to the mechanism of the discharge It will be necessary, therefore, in further work in this direction, to adopt random time bases checked against a continuously calibrated oscillator

VI —*Definitions and Limits*

1 *General* —The minimum field strength detectable with normal operating constants and single-stage amplification, with which all the determinations of the series were made, is of the order of 4 millivolts per metre. The definition of "duration" implied by this experimental limit is thus "that period during which the field change due to the discharge exceeds 4 millivolts per metre" The criterion of aperiodicity is, similarly, the absence of any reversed field change exceeding 4 millivolts per metre In considering mean values, it should be recollected that the mean field strength emerging from the statistical reduction will be reduced, on one hand, by the fact that field changes exceeding 0 5 volts per metre carry the indicating spot off the screen when a unit capacity ratio is in use The occurrence of many such changes in any one period was met by change of coupling capacity, but isolated large discharges would escape measurement and the statistical mean will be slightly too low on this account On the other hand, there is a relatively large number of disturbances, the field strength of which lies above that produced by average radiotelegraphic signals, but below the limit of 4 millivolts per metre, the neglect of such disturbances will raise the computed mean value The opposing sense of these departures, and the infrequency of large disturbances, justify the presentation of the computed means as fairly representative of that range of atmospherics whose peak field changes exceed 1 or 2 millivolts per metre

2. *Main Classification* —As in the preceding paper, the disturbances are grouped in two main types, governed by the criterion of aperiodicity specified, and called the Aperiodic, or A type, and the Quasiperiodic, or Q type, respectively. Those members of the main types which are associated with a discharge

governed by the time constant of the grid circuit, and so appear to have a sensible electrostatic term, are prefixed S P, an S P A thus being a sensibly aperiodic atmospheric with an apparent semi-permanent field change

The convention as to sign is, as in the preceding paper, that the positive sign is allotted to discharges the absolute peak voltage of which is such as to make the aerial terminal of the coupling condenser positive with respect to earth The sign of the discharge is taken as that of its greatest peak, irrespective of the incidence in time of that peak relative to any secondary peaks

3 *Sub-classification and Characteristic Ratios*—The main types are subdivided according to two criteria, firstly according to the "rounded" or "peaked" character discussed in the earlier paper, and secondly, according to the relative duration of the growth and decay periods in the aperiodic type, and to the sequence of opposite peaks in the quasiperiodic type A disturbance is classed as "rounded" if its slopes are, on the whole, convex outwards, *i e*, if the greatest rate of change of field occurs near the zero line, and conversely the "peaked" class has its slopes concave outwards, the greatest rate of change being near the point of maximum departure from the quasi-steady field strength

The unambiguous determination of temporal relations by means of the unidirectional time-base also allows of a fuller investigation of the three characteristic ratios introduced in the earlier discussion

For the aperiodic type, the "Slope Ratio" may now be defined as the ratio of the duration of the decay period to that of the growth period, *i e*, the ratio of the time interval between the maximum field change and the succeeding return to zero to the interval between the departure from zero and the attainment of maximum field change Thus the slope ratio will be unity for a symmetrical peak, less than unity for a discharge in which the (early) period of growth to maximum exceeds the (later) period of decay to zero, and conversely The sign of the slope ratio is that of the peak concerned

For the quasiperiodic type, the Peak ratio is defined as the amplitude ratio of the earlier departure to the next following departure of opposite sign (It is convenient, though loose, to call these departures "half-cycles," and this will be done throughout the discussion, with the reservation that a strictly cyclic character is likely to be very rare in these disturbances) The sign of the peak ratio is that of the earlier half-cycle, a quasiperiodic discharge with N half-cycles will have N − 1 peak ratios alternating in sign A peak ratio exceeds unity when the half-cycle which is earlier in time is greater in amplitude than its successor

The "Cycle Ratio" for quasiperiodics is defined as the ratio of the duration of the earlier half cycle to that of its successor, the sign being that of the earlier half cycle

The quantities involved and the conventions adopted having been specified, the results of the statistical reduction may now be detailed

VII —*Experimental Results*

1 *Preliminary*—The first series, recorded in the previous paper, yielded values of the principal constants which were as shown in the first line of Table I, to be discussed later in this paper The presence in the A — class of many discharges the duration of which was known to be incorrectly represented by the oscillographic deflection (discharges which are for convenience referred to in discussion as S P A s) vitiated the mean duration for that class, which becomes 2,065 microseconds (in place of 4,625 microseconds) when the fallacious "durations" of S P.A 's are eliminated from the series

Table I

Series	Number observed.							
	A +	A —	A	Q +	Q ±	Q —	Q	Total.
1	38	225	263	105	73	120	298	561
2	365	501	866	56	49	135	240	1,106
3	340	255	595	68	10	44	122	717
4	2 654	1,454	4,108	683	350	290	1,323	5,431
	3 397	2,435	5,832	912	482	589	1,983	7,815

Series	E^{mr}/m							
	A +	A -	A	Q +	Q ±	Q —	Q	Total
1	50	108	100	200	70	100	128	115
2	53	100	80	304	249	365	221	122
3	32	49	39	64	87	92	76	46
4	76	80	77	115	197	125	139	92
	69	83	75	183	181	170	156	95

Table I --*continued*

Series	Duration μs							
	A +	A −	A	Q +	Q ±	Q −	Q	Total
1	1,475	2,065	1,980	2,075	1,925	1,800	1,925	1,950
2	1,510	2,375	2,010	2,840	2,480	2,850	2,770	2,175
3	3,070	3,625	3,310	5,580	5,670	5 440	5,535	3,690
4	2,015	2,665	2,245	3,480	2,400	3,680	3,240	2,485
	2,060	2,650	2,310	3,435	2,405	3,240	3,125	2,515

The corresponding results of the second series are tabulated in line 2 of Table I Here S P A 's of both signs were present, and their removal from the means produces a satisfactory agreement between the mean durations for the aperiodic classes in the two series The values for duration of A + were 1,475 and 1,510 microseconds respectively, of A − 2,065 and 2,375 microseconds The Q classes, however, show an increase of mean duration amounting to between 25 and 50 per cent

This increase is even more marked in third series, the mean durations of which (line 3) are all two or three times as great as in the preceding series We shall revert to these differences, and their relation to the results of the larger fourth series (line 4) at a later point in the discussion

The principles of sub-classification set out in VI having been applied to the individuals of this fourth and main series, Table II exhibits the results of the allocation according to types, and the mean and modal values of the two principal parameters, duration and peak field strength, for each type Table IIIA shows the numerical distribution according to the type of asymmetry present, while Table IIIB shows the relations of the principal parameters to the "rounded" or "peaked" character of the wave form, and to the order of incidence of the half-cycles

Some of the salient features of these tables, and of the analysis on which they are based, will now be discussed For convenience, values for Series 4 have also been re-grouped into two tables, IV and V, corresponding respectively to Tables I and II of the previous communication.

Table II.

APERIODIC	−		Typical Appearance		a	b	c	d	e	f	Indeterminate g	Total All A −
			Number		126	395	236	46	344	195	32	1454
			Duration μs	Mean	2245	2580	2730	2560	2920	2450	3180	2665
				Mod Freq	1750	1350	2250	1500	1750	1400		1600
			Field Strength v/m	Mean	0·087	0·054	0·138	0·087	0·06	0·054	0·108	0·08
				Mod Freq	0·07	0·03	0·06	0·06	0·04	0·04	0·06	0·060
	+		Typical Appearance		a	b	c	d	e	f	g Indeterminate	Total All A +
			Number		594	786	487	118	346	294	29	2654
			Duration μs	Mean	1750	2295	2040	1720	2030	1960	1770	2015
				Mod Freq	1300	1700	1600	1350	1350	1200		1750
			Field Strength v/m	Mean	0·105	0·045	0·103	0·104	0·05	0·056	0·103	0·076
				Mod Freq	0·06	0·03	0·06	0·07	0·04	0·04	0·05	0·055
QUASI - PERIODIC	−	Greater Voltage First	Typical Appearance		a	b	c	d	e	f	Indeterminate g	
			Number		122	49	57	5	1	2	15	
			Duration μs	Mean	3240	2120	4310	4900	5230	9340	5130	
				Mod Freq	1800	2000	3200					
			Field Strength v/m	Mean	0·13	0·17	0·088	0·17	0·25	0·08	0·14	
				Mod Freq	0·09	0·16	0·045					
		Greater Voltage Later	Typical Appearance		h	i	j	k	l	m	Miscellaneous n	Total All Q −
			Number		6	4	12	6	6	3	2	280
			Duration μs	Mean	3900	1350	4510	6220	6240	7290	7290	3680
				Mod Freq								2300
			Field Strength v/m	Mean	0·07	0·11	0·076	0·15	0·11	0·16	0·16	0·125
				Mod Freq	0·05		0·04					0·075
	+	Greater Voltage First	Typical Appearance		a	b	c	d	e	f	Indeterminate g	
			Number		375	28	81	14	1	0	24	
			Duration μs	Mean	3180	2570	4070	5530	7250		4000	
				Mod Freq	2450	1500	2750					
			Field Strength v/m	Mean	0·12	0·10	0·07	0·17	0·07		0·09	
				Mod Freq	0·075	0·14	0·035					
		Greater Voltage Later	Typical Appearance		h	i	j	k	l	m	Miscellaneous m	Total All Q +
			Number		50	13	37	32	15	1	2	683
			Duration μs	Mean	3180	2420	3450	4930	4620	3130	5295	3460
				Mod Freq	1700	2300	3000	5800	4700			2400
			Field Strength v/m	Mean	0·12	0·10	0·075	0·14	0·08	0·12	0·12	0·118
				Mod Freq	0·075		0·04	0·12	0·04			0·07

QUASI - PERIODIC	±1	Typical Appearance		a	b	c	d	e	f	g	h	Indeterm. i	Total All Q ±
		Number		205	77	5	24	3		7	6	21	350
		Duration μs	Mean	1910	2190	4210	3450	4470		4730	4150	5080	2400
			Mod Freq	1250	1450		3500						1250
		Field Strength v/m	Mean	0·19	0·25	0·16	0·20	0·17		0·07	0·04	0·19	0·197
			Mod Freq	0·16	0·15		0·25			0·05	0·05		0·17

Table IIIA

	Slope ratios						Total
	< 1		1		> 1		
Form as in Table II	*d* & *f*		*a* & *b*		*c* & *e*		
	Number	Percentage	Number	Percentage	Number	Percentage	
A	241	1 3	521	37 1	640	45 6	1 402
A +	412	15 7	1 380	52 6	833	31 7	2 025
A both signs	653	16 1	1 901	47 3	1 473	36 6	4 027

	Peak ratios						Total
	< 1		1		> 1		
Form as in Table II	*h* to *m*		Q ± *a* to *h*		*a* to *f*		
	Number	Percentage	Number	Percentage	Number	Percentage	
Q	37	6 2	329	54 6	236	39 2	602
Q +	148	15 0	329	33 3	509	51 7	986
All Qs	185	14 7	329	26 1	745	59 2	1 259

Table IIIB

—	Form, of Table II	—	Number observed	Duration µs.		Field strength. v/m.		Slope ratio			
				Mean	Most frequent.	Mean	Most frequent	Mean	Most frequent		
A − Peaked A − Rounded	*a, c, d* *b, e, f*		468 934	2,590 2,680	2,100 1,700	0·123 0·056	0·060 0·035	3·62 1·32	1·0 1·0		
A + Peaked A + Rounded	*a, c, d* *b, e, f*		1,199 1,426	1,865 2,160	1,350 1,600	0·104 0·051	0·07 0·032	2·01 1·23	1·0 1·0		
								Peak ratio.		Cycle ratio.	
								Mean.	Most frequent.	Mean.	Most frequent.
Q − Peaked	*a, b, d, f*	Greater voltage first	178	3,045	1,740	0·142	0·13	4·37	3·1	1·1	1·0
Q − Rounded	*c, e*		58	4,325	3,200	0·066	0·045	3·3	2·2	2·0	1·7
Q − Peaked	*h, i, k, m*	Greater voltage later	19	4,755	—	0·118	0·05	0·35	0·25	1·17	1·0
Q − Rounded	*j, l*		18	5,085	—	0·067	0·04	0·36	—	0·9	—
Q + Peaked	*a, b, d, f*	Greater voltage first	417	3.215	2,550	0·126	0·075	5·75	4·5	1·02	1·0
Q + Rounded	*c, e*		92	4,110	2,750	0·07	0·035	3·7	2·8	1·85	1·6
Q + Peaked	*h, i, k, m*	Greater voltage later	96	3,660	2,400	0·134	0·09	0·29	0·19*	0·95	1·0
Q + Rounded	*j, l*		52	3,845	4,000	0·079	0·04	0·34	0·30	0·92	1·0
Q ± Peaked Q ± Rounded	*a, b, c, d, e, f* *g, h*		314 15	2,120 4,420	1,350 —	0·204 0·035	0·17 0·03	1·0 1·0	1·0 1·0	0·94 0·93	1·0 1·0

Table IV —*Characteristics of the Main Types*

—	Number observed	E^{m} /m. Mean	E^{m} /m. Mode	E^{m} /m. Maximum observed	Durations μs Mean	Durations μs Mode	Durations μs Maximum observed.	Peak ratio
A +	2,654	76	55	500	2,015	1,750	23,500	
A −	1,454	80	60	670	2,665	1,600		
A both signs	4,108	77	60		2,245	1,700		
Q +	683	115	70	500	3,480	2,400	12,000	3.09
Q ±	350	197	170	530	2,400	1,250	11,800	
Q −	290	125	75	400	3,680	2,300	10,600	3.48
All Q s	1,323	139	70		3,240	2,050		

Table V

—	Number observed				Mean E^{m} /m.				Mean duration μs			
	+	±	−	Total	+	±	−	Total	+	±	−	Total
A Peaked	1,199	—	468	1,667	104	—	123	109	1,865	—	2,580	2,065
A Rounded	1,426	—	934	2,360	51	—	56	53	2,160	—	2,680	2,365
Q Peaked	513	314	197	1,024	128	204	140	154	3,300	2,120	3,210	2,925
Q Rounded	144	15	76	235	74	35	86	75	4,015	4,420	4,505	4,200
A	2,625	—	1,402	4,027	75	—	78	76	2,025	—	2,645	2,240
Q	657	329	273	1,259	116	197	125	141	3,455	2,225	3,570	3,160
Peaked	1,712	314	665	2,691	111	204	128	126	2,295	2,120	2,765	2,390
Rounded	1,570	15	1,010	2,595	53	35	58	55	2,330	4,420	2,815	2,530

2. *The Aperiodic Type.*—Of the 5,674 atmospherics observed in series 4, 4,351 were aperiodic in type. This number included 243 discharges, the apparent duration of which exceeded 10,000 microseconds. This duration has been adopted as the boundary between aperiodics A of normal type and those, S.P.A., in which the duration of the oscillographic deflection was governed by the time constant of the grid circuit. This limit has been adopted on two grounds. In the first instance, a limit of 30,000 microseconds was adopted as being that set by the mean time constant of the grid circuit. On the drawing of the frequency curve for aperiodic discharges with a slow quasi-exponential decay, a well-marked minimum ordinate was found at 9,000 microseconds, succeeded by a secondary rise beyond 10,000 microseconds. This was accepted as indicating that the discharges exceeding 10,000 microseconds in duration belong to a different class, probably S.P.A.'s observed at times when the grid circuit time constant was temporarily below normal. The limit was therefore readjusted to 10,000 microseconds. The actual choice of limit is not of prime importance, the change from 30,000 microseconds to 10,000 microseconds resulting in a transfer of 71 discharges to the S.P.A. class (previously containing 72 discharges of apparent duration between 0.03 and 0.07 seconds, and 100 exceeding 0.07 seconds), and reducing the mean duration of the "normal" class from 2,555 to 2,245 microseconds. The true limit, variable on account of variations of insulation resistance with weather conditions, lies between the two discussed. There is no doubt that discharges with a true duration over 10,000 microseconds occur, observations on the potential differences produced across the aerial damping resistance with the condenser removed from the circuit (dE/dt method) having shown true durations, of sensibly continuous discharges, up to 20,000 microseconds.

The mean peak field change in the S.P.A. class amounted to 0.32 volts per metre. This is a roughly approximate value only, since small semi-permanent changes are difficult to observe and interpret, being readily confused with the displacements due to slowly varying "aerial current," and since the extreme excursion is difficult to observe in the case of larger deflections. The order of magnitude is, however, in accordance with the interpretation placed on the S.P.A. class.

Coming to the "normal" aperiodic type, containing aperiodic discharges without any apparent electrostatic terms, the total number observed reached 4,108, of which 2,654, or 65 per cent., had positive sign, 1,454 being negative.

The "mean" aperiodic atmospheric had a peak field strength of 77 millivolts per metre, and a duration of 2,245 microseconds. The mean values for positive aperiodics were 76 millivolts per metre and 2,015 microseconds, for negatives 80 millivolts per metre and 2,665 microseconds The most frequently occurring field strength in each class was 55 millivolts per metre for the positives and 60 millivolts per metre for the negatives, the most frequently occurring duration 1,750 microseconds for positives, 1,600 microseconds for negatives

The mean slope ratio for all normal aperiodics, irrespective of sign, was 1 96, *i e*, the decay period occupied practically two-thirds of the total duration of the discharge. The slope ratio was notably greater for negative disturbances than for positives, the respective values being 2 21 and 1 79

Of the determinable forms 1,380 (53 per cent) of the positive and 521 (37 per cent) of the negative aperiodics were symmetrical, 412 (16 per cent) of the positives and 241 (17 per cent) of the negatives had a slope ratio less than unity

Of the total number of normal aperiodics, 2,360, or 57 per cent, were of the "rounded" form, while 1,667, or 41 per cent, were "peaked," the remaining 81 (2 per cent) being of an intermediate type, usually so strongly rippled as to prevent allotment in this classification The positive aperiodics were approximately evenly divided amongst the two classes, 1,426 (54 per cent) being rounded, 1,199 (45 per cent) peaked. The negatives comprised 934 (64 per cent) rounded and 468 (32 per cent) peaked The mean peak field strength of the peaked class was 109 millivolts per metre, that of the rounded class 53 millivolts per metre, a ratio of 2 06 The mean durations were 2,365 microseconds for rounded and 2,065 microseconds for peaked forms

The mean slope ratio of the rounded class was 1 3, 50 per cent of this class being strictly symmetrical, while the peaked class had a slope ratio of 2 5, with 43 per cent symmetrical

3 *The Quasiperiodic Type*—The number of quasiperiodic disturbances observed was 1,323, or 24 per cent of the total number of normal field changes Of these, 683 (or 52 per cent.) were of predominantly positive sign, 290 (22 per cent) negative, and 350 (26 per cent) had equal and opposite peaks The mean quasiperiodic atmospheric of the series had a peak field strength of 139 millivolts per metre, and a duration of 3,240 microseconds. The mean values for the positive class were 115 millivolts per metre and 3,480 microseconds, for the negative 125 millivolts per metre and 3,680 microseconds, and for the Q ± class 197 millivolts per metre and 2,400 microseconds

The half-cycle of greater amplitude normally, but by no means invariably, preceded the smaller half-cycles. Of the completely determinable Q forms, 80 per cent. had their maximum half-cycle first, the percentage being higher for negatives (87 per cent) than for positives (78 per cent). In 6 per cent of the total (in 7 per cent of the Q + class, 4 per cent. of the Q − class), the half-cycle of greatest amplitude was both preceded and followed by smaller half-cycles

The majority of disturbances of the Q class consisted of a large peaked half-cycle associated with a smaller rounded half-cycle, such forms constituting 59 per cent of all quasiperiodics whose peak ratio differed from unity The next most numerous class, constituting 21 per cent of the total, had both half-cycles rounded, while in 10 per cent of the total both half-cycles were peaked In the Q ± class, 95 per cent had the half-cycles of equal amplitude peaked, only 5 per cent being rounded

Forms in which the principal half-cycle was peaked formed 76 per cent of the total, 72 per cent of these being positive and 28 per cent negative , rounded forms, 22 per cent. of the total, were divided into 65 per cent. positive and 35 per cent negative

The mean peak ratio amounted to 4 3 in the case of positive quasiperiodic (4 8 for peaked and 2 5 for rounded) and to 3 6 (4 0 for peaked and 2·6 for rounded) in the case of negatives

The mean cycle ratio similarly was 1·1 in the case of positive quasiperiodics (1 0 for peaked and 1 5 for rounded) and 1 3 (1 1 for peaked and 1 7 for rounded) in the case of negatives

4 *The Relations of the Types* —The principal constants of the "normal" forms, after exclusion of S P.A 's from the four series, are collected in Table I, and their differences will call for some remark The last line of Table I gives grand means, comprising the results of nearly 8,000 individual measurements, of the principal constants. These may be taken as based on an adequate number of samples, and thus as being fairly typical of British autumnal atmospherics

It will be noted that the mean durations are greater in the second series than in the first, much greater in the third, and in the fourth series assume values intermediate between those of the second and third series. This is probably, to some considerable extent, due to seasonal variations, but there can be little doubt that a main cause is insufficient care, in the earlier series, in ensuring even sampling The effect of choice of time base on the mean duration observed is well shown by the analysis of series 4 The mean number of atmospherics observed per quarter-hour on each time base, and the mean duration of the atmospherics observed on each base, were as shown —

Time base—					
Frequency	85	128	256	512	1,000 ~
Duration	11,760	7,820	3,910	1,950	1,000 μs
Number per quarter-hour	38	36	30	23	26*
Mean duration .	3,490	2,810	1,980	1,580	1,260 μs

Thus the mean duration tends towards comparability with that of the time base used, though the slowness of the variation with base is a sufficient indication that in this series the range of bases used was adequate. But the neglect of the lower frequencies in the first series certainly gave far too much weight to the relatively infrequent short duration discharges. This was realised to some extent in the second series, and on the introduction of the linear time base a deliberate effort was made, in series 3, to redress the balance by concentrating attention on bases of the order of 0·01 and 0·02 seconds. This, in part, at least, accounts for the great increase in mean duration in the short series 3. The unweighted average of these three early series is in satisfactory agreement with that of the well-balanced series 4. On the whole the mean durations will now be somewhat too low, owing to the erroneous inclusion of some "normal" discharges of long duration in the S.P.A. class.

The most prominent feature of the durations, in all series, was the greater mean duration of quasiperiodic as opposed to aperiodic discharges, the excess amounting to 35 per cent. of the mean duration of the A type on the Grand Mean. The greater duration of the negative aperiodics as against positives was also prominent in all series, and amounts to 29 per cent. of the A + duration on the Grand Mean. There was no corresponding divergence amongst the Q's, the only marked feature of their durations was the relative brevity of the Q ± class, which was prominent only in series 4, where it arose from the high relative frequency of the sub-class consisting simply of two equal and opposite "peaked" half-waves, each of short duration.

The next most prominent divergence amongst the series is in the relative numerical frequency of occurrence of the various types. Series 1 showed a great preponderance of A − over A +, but this preponderance decreased and finally reversed as observations continued. No explanation other than seasonal variation, and inadequate sampling in the brief series 1, presents itself. The same may be said of a change from approximate numerical equality of A's and Q's in series 1 to a 3 to 1 preponderance of A's in series 4, and in the grand totals. These divergences were noted on their appearance during the actual observations of series 2 and 3, the observers were thus early aware of this tendency to diverge from the relations of series 1, and were consequently careful to guard against unconscious selective preferences A further noteworthy feature of the relative frequency of occurrence of A's and Q's was that the Q's were relatively infrequent in discharges of short duration Thus the ratio of number of aperiodics to number of quasiperiodics observed on the standard bases were as under —

---

* The base of 1,000 μs was not used during the less disturbed latter half of this period.

Base	11,760	7,820	3,910	1,950	1,000 μs
Ratio $\frac{A}{Q}$	1·7	2·4	4·5	6·0	8·0

This variation is, of course, simply another aspect of the fact that the mean duration of the Q was considerably greater than that of the A

No very profound modifications in the order of relative field strength occur in passing from series 1 to series 4, the omission of the essentially strong S P A 's from the A − mean in the final series reduces that mean to close agreement with that for the A + class, and the Q ± class rises to a leading position as regards mean field strength

To summarise, we had the sensibly aperiodic discharge appearing nearly three times as frequently as the quasiperiodic, and the positive discharge, both amongst aperiodics and quasiperiodics, occurring half as frequently again as the negative The quasiperiodic discharge, with its mean peak field strength of 0·156 volts per metre, had almost precisely twice the amplitude of the aperiodic, with its 0·075 volts per metre The negative discharge of both types was some 20 to 30 per cent greater in amplitude than the corresponding positive The negative aperiodic had a mean duration exceeding that of the positive by a percentage (28 per cent) which, on the whole mass of data, is comparable with its percentage amplitude excess (20 per cent) The positive quasiperiodic had a duration very slightly in excess of the negative, the mean quasiperiodic had a duration a third greater than had the mean aperiodic

The mean maximum field strength of peaked aperiodics was 2·06 times that of rounded aperiodics, the corresponding ratio for quasiperiodics was 2·05.

The most frequently occurring individual form of atmospheric was a symmetrical "rounded" positive aperiodic, a form assumed by 14 per cent. of all atmospherics of series 4 Eleven per cent. were symmetrical "peaked" positive aperiodics, 9 per cent. were peaked positive aperiodics with a decay period 3½ times as long as the growth period, while 7½ per cent were quasiperiodics with a peaked positive half-cycle followed by a rounded half-cycle of almost identical duration but of one-fourth the amplitude. Rounded aperiodics, of both signs, with decay periods twice as long as the growth period, symmetrical rounded negative aperiodics, and peaked negative aperiodics with slow decay (five times the growth period), each contributed about 6 per cent. of the distribution, while the only notable class with a growth period exceeding the decay period was that of the rounded positive aperiodics with a slope ratio of ½, which formed 5 per cent. of the total distribution.

Of the quasiperiodics, 9 per cent. had three or more half-cycles, ½ per cent. had four half-cycles.

5. *Relations referred to Sign.*—It is convenient to collect in a single paragraph the characteristics which depend particularly on the sign of the principal field change, even although this involves repetition.

It may be desirable, in the first instance, to dismiss the quantities which are not conspicuously dependent on sign. There is no marked preference, amongst the A's, for a steep slope of increasing positiveness, the number having such a slope being 1,074, as against 1,052, with the slope of increasing negativeness the steeper. So also in quasiperiodics the number in which the first half-cycle is positive is 655, as against 604, in which the first half-cycle is negative.

The relative numbers of positive aperiodics to negative aperiodics are as 1·8 to 1; for quasiperiodics (omitting the Q ± class) this ratio is 2·4 to 1. The mean peak voltage of negative aperiodics is 1·05 that of the positives; for quasiperiodics the ratio is 1·09. The mean duration of negative aperiodics is 1·32 that of positives; for quasiperiodics the ratio is 1·05.

The mean negative aperiodic is much less symmetrical than the mean positive, 53 per cent. of positives being symmetrical, while only 37 per cent. of negatives are so. The mean slope ratio for negatives is 2·1, that for positives is 1·6.

In general it may be stated that a disturbance with negative termination is of greater duration than the corresponding form with reversed sign. This is true in respect of durations and slope ratios in aperiodics, and also in respect of durations in quasiperiodics.

6. *Relations referred to Form.*—Dealing similarly and summarily with relations in which the form of the wave is involved, it will be seen that amongst the aperiodics the number of rounded forms is in the ratio of 1·4 to 1 to peaked forms; the corresponding ratio for quasiperiodics is the very small one of 0·23. The mean peak field strength for peaked aperiodics is 2·06 times that for rounded aperiodics; the corresponding ratio for quasiperiodics is 2·05. The mean duration for rounded aperiodics is 1·14 times that for peaked; the corresponding ratio for quasiperiodics is 1·44.

Amongst quasiperiodics the first half-cycle is peaked in 73 per cent. of cases.

The numerical ratio of peaked to rounded forms is greater for negative than for positive signs, both in the case of aperiodics (1·99 to 1·19) and quasiperiodics (0·38 to 0·28).

7. *Unit Durations.*—It is of interest to investigate the relative mean durations of the individual "half-cycle" forms which appear, in varying combinations, amongst the quasiperiodic discharges. Thus, a quasiperiodic discharge consisting of a half-cycle of large amplitude, which may be rounded or peaked, associated with one or more smaller half-cycles of one form or the other, the question arises whether a large peaked half-cycle, for example, retains a characteristic duration independent of its associations. A further question of importance is whether this characteristic duration, if it exists, is comparable with the duration of the so-called "aperiodic" discharge of similar general form.

The mean values of durations have accordingly been computed for each class, and the results are exhibited in Table VI. It will at once be seen that the various forms of half-cycle do possess characteristic constants of duration which are comparatively insensitive to their associations. In descending order of mean duration the eight forms of half-cycle fall into the following sequence, viz., large rounded negative, large rounded positive, small rounded positive, small rounded negative, large peaked positive, small peaked negative, large peaked negative, small peaked positive, or symbolically, the order of decreasing mean duration is

$$\mathrm{R}\,-,\ \mathrm{R}\,+,\ r\,+,\ r\,-,\ \mathrm{P}\,+,\ p\,-,\ \mathrm{P}\,-,\ p\,+,$$

the mean duration of R − being twice that of $p\,+$. Within the individual groups, however, it will be seen that the duration of $r\,-$, for example, varies from a minimum of 1,430 when it occurs in form Q + 1 (see Table II) to a maximum of 2,200 in form Q − *m*, a ratio of only 1·5 between maximum and minimum. The other typical half-cycles show a similar consistency in duration, whatever the form of quasiperiodic disturbance in which they occur. The peak field strength values, which might, *a priori*, have been expected to show much less regularity, are in fact scarcely inferior to the duration values in this respect. P + having a mean peak value lying between 119 and 176 *mv/m*, P − 110 to 165 *mv/m*, R − 76 to 83 *mv/m*, with exceptions in classes too small to be fair samples, and R + 67 to 90 *mv/m*. Again, the standard deviations follow the mean values, but are even more steadily characteristic of the half-cycle and insensitive to circumstances.

The relation between the nominally aperiodic disturbance and the half-cycle of the quasiperiodic may be seen from Table VII in which line "Q" repeats

Table VI

Form (*cf* Table II) Q +	No.	+ P	+ R	− *r*	− *p*	+ *r*	Form (*cf.* Table II) Q −	No	− P	− R	+ *r*	+ *p*	− *r*
a	375	1,540		1,640			*a*	122	1,350		1,890		
b	28	1,100			1,470		*b*	49	1,070			1,050	
c	91		2,330	1,740			*c*	57		2,640	1,670		
h	50	1,510		1,670			*h*	6	1,730	2 590	2,170		
i	13	1,230			1,190		*i*	4	1,020			930	
j	37		1 680	1 770			*j*	12		2 350	1,920		
d	14	1,780		1,770		1,980	*d*	5	1,100		1,690		2,110
e	1		3,300	1,850		2,800	*e*	1			1,180 3,250		1,700
	0						*f*	2	2,030		2,030		2,030
k	32	1,510		1,550 1,870			*k*	6	2,030		1,900 2 270		
l	15		1,880	1,430 1,510			*l*	6		2 180	2,190 1,870		
m	1	470		1,000		1,720	*m*	3	2,540		2,550		2,200
No		513	144	663	41	16	No.		197	76	234	53	11
Mean		1,503	2,123	1,665	1,288	2,014	Mean		1,326	2,592	1,876	1,042	2,061

Table VII.

—	R −	R +	P −	P +
Q	2,590	2,125	1,325	1,505
A	2,680	2,160	2,580	1,865

the mean durations found for the principal half-cycles, while line "A" contains the mean durations of all aperiodics of rounded and peaked form respectively, according to sign It will be seen that except in the negative peaked class the mean duration of the aperiodic is of the same order as that of the principal half-cycle of similar form in the quasiperiodic, the agreement being very close indeed in the case of the rounded form

The origin of the difference in the case of the peaked forms is obscure, but it is accentuated in the case of the Q ± class, in which, as has been noted, the total durations of peaked forms are exceptionally small, while the rounded forms are comparable in duration with the asymmetric forms In respect of peak field strengths the relations between aperiodics and quasiperiodics already referred to on p 644 should be noted in their bearing on the "half-cycle" relations here discussed.

8 *The Fine Structure of Atmospherics* —It was remarked in the preliminary paper that in some 7 per cent of the forms then delineated, "ripples," the amplitude of which reached 10 per cent of the fundamental amplitude, had been observed It was, from the beginning, clear that the fine structure of the atmospheric, of which these ripples were the extreme cases, was of fundamental importance in relation to interferent properties, and the results of further observations in this direction are, therefore, specially important

Two methods are available for the study of fine structure—firstly, the delineation of such structure as can be detected in the curves of field change on the standard capacity-coupled circuit when time bases of short period are used, and secondly, the special examination of rate of change of field by the resistance-coupled circuit which gives curves the ordinates of which are proportional to dE/dt. The latter method will obviously give oscillograms in which the amplitude of the fine detail is much enhanced relatively to the fundamental, and, in fact, it is found extremely difficult to make use of the "dE/dt" circuit in practice, owing to the extreme complexity of the oscillograms obtained. This is particularly unfortunate in view of the extreme simplicity of the circuits involved in the

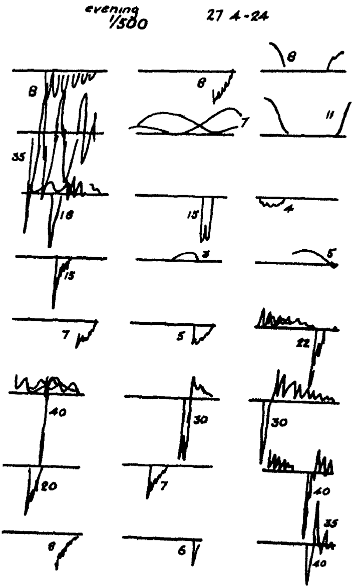
"dE/dt" method, and of the very direct applicability of dE/dt as a measure of interferent properties. Much can be done immediately towards the study of fine structure by this method by increase of resolving power even at the expense of loss of sensitivity, and special experiments are now being undertaken with oscillographs designed for increased brilliancy of fluorescence, so that the limiting speed of translation of spot for clear visibility may be raised.

Reverting to the direct study by the "E" method, it was found that, of the 1,210 atmospherics in series 4 which were observed on time bases sufficiently rapid for resolution (*i.e.*, on bases of 1,950 μs and 1,000 μs), 212, or 17 per cent., contained ripples of period under 500 μs and amplitude over 0.002 volts per metre. The total number of measurable ripples contained in these 212 forms amounted to 1,130, the most frequently occurring ripple period was 100 μs, the mean period 160 μs with a standard deviation from mean duration of about 80 μs. The shortest period ripple observed was 30 μs. The greatest number of ripples observed in one train was 22, while the longest period observed to be continuously occupied by ripples of the magnitude specified was 3,100 μs.

The total field change constituting a ripple is taken, for the purpose of this reduction, as the sum of the two opposite departures from the smoothed fundamental curve, *i.e.*, as the ripple, isolated from the slope of the fundamental. The absolute maximum field change constituting an observed ripple was 0.23 volts per metre, the mean of the maximum ripples in each of the 212 trains was 0.027 volt per metre.

The mean relative amplitude of ripples, defined as the ratio of the maximum total field change constituting the ripple, as above defined, to the maximum field change constituting the fundamental aperiodic discharge or the fundamental half-cycle on which the ripples appeared, was again of the order of 10 per cent.

While the figures cited are typical of the worst cases of gross ripple structure experienced in England in autumn, they are far from typical of the general fine structure of atmospherics, whether in England or abroad. For a fuller picture one must have recourse to measurements of dE/dt, and must consider also typical oscillograms of E and dE/dt in tropical regions, where, particularly in dark hours, the fine structure assumes great prominence, even on the "E" oscillograms. Some typical oscillograms are reproduced as figs. 9 to 11. Figs. 9 and 10 show two random groups of untouched drawings from observations at Khartoum on April 18th, 1924, on the "E" circuit with a time base of 1,000 μs. Fig. 11 shows a corresponding group for April 27th, 1924, on the same circuit, with a time base of 2,000 μs.


evening
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40

Fig 9

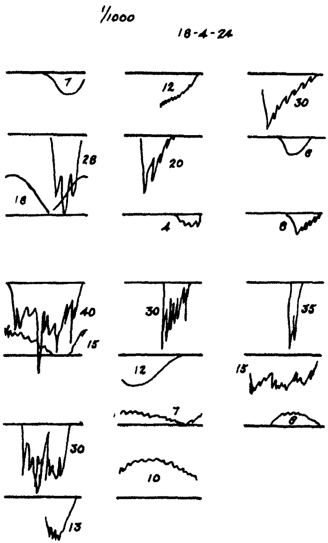

Fig. 10

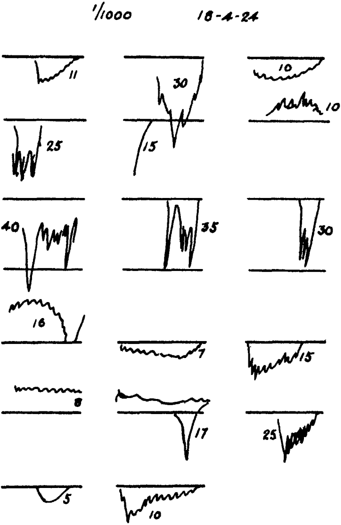

FIG. 11

† Thanks are due to the Department of Scientific and Industrial Research, which, on the advice of its Radio Research Board, provided facilities for the work described, and accorded permission to publish the results

Summary

1 The paper describes the development of work, reported in an earlier communication, on the oscillographic examination of the characteristics of atmospheric electric disturbances of short duration The method now involves the use of a cathode-ray oscillograph with a time-base which is both uniform in scale and unambiguous as to time-sense The apparatus and methods described include a series of station-tests for checking the performance of the assembly The basis of the methods used is re-discussed

2 Statistical analyses of approximately 8,000 individual drawings of atmospheric wave forms are tabulated and summarised A more detailed sub-classification is based on the improved discrimination afforded by the unambiguous time-base Sensibly aperiodic discharges were three times as numerous as were quasiperiodics, predominantly positive discharges were one-and-a-half times as numerous as were negatives The mean quasiperiodic had a peak field strength of 0 156 *v/m*, the aperiodic 0 075 *v/m* The negative discharges of both types were stronger by 20 per cent to 30 per cent than the positives The mean quasiperiodic had a duration 3,125 μs, 30 per cent greater than that of the mean aperiodic

The most frequently occurring form of atmospheric was a symmetrical rounded positive aperiodic, forming 14 per cent of the whole distribution The most frequent quasiperiodic, forming $7\frac{1}{2}$ per cent of the distribution, had a peaked positive half-cycle followed by a single rounded negative half-cycle

3 Examination of the fine structure of atmospherics shows a frequent "ripple period" of the order of 100 μs Typical oscillograms of fine structure as observed in dark hours in the Tropics are reproduced

On the Nature of Atmospherics —III.

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J F. Herd, A.M.I E E

(Communicated by Sir Henry Jackson, F.R.S —Received April 23, 1926)

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I —*Introduction.*

The present paper continues the account of investigations on the nature of atmospherics given in papers I and II[*] of similar title As the argument is essentially continuous from paper II to paper III, the numbering of equations, tables and figures has been made to run continuously from the former to the latter paper

II —*Semi-Permanent Field Change Determinations*

As has been mentioned in the preceding paper, the cathode-ray oscillograph assembly may be used for the determination of the sign and magnitude of net changes of the earth's electric field, and when thunderstorms were not far distant measurements of such changes were made at Aldershot and Helwan by this method, which will be referred to as method A The magnitude of the field changes was calculated with the aid of equation (9)

These observations were supplemented by data obtained using two other methods in which the sign and magnitude of the charge on an exposed conductor, released by the destruction of the thundercloud moment, were measured by a capillary electrometer (method B) and by a string electrometer (method C). The capillary electrometer was of the type first described by Prof C T R Wilson,[†] and used by him in determinations of the semi-permanent changes of field produced at short distances from lightning discharges, and consists of a small bubble of dilute sulphuric acid enclosed by mercury in a horizontal capillary tube The displacement of the sulphuric acid bubble, which is observed by means of a microscope, is proportional to the *quantity* of electricity passing through the electrometer. In the electrometer used the displacement of the meniscus was 1 mm per $5 \cdot 5 \times 10^{-8}$ Coulomb which under magnification gave 1 eye-piece division per $3 \cdot 6 \times 10^{-9}$ Coulomb. The electrometer thus measured the charge (Q) passing down the aerial as a result of the field change, and thus formula (8) is applicable But since the capacity of the capillary electrometer C_1 may be regarded as infinite compared with C_0 the equation may be further simplified to

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[*] 'Roy. Soc. Proc.,' A, vol. 103, p. 84 (1923), and vol. 111, *supra* (1926).

'Roy Soc. Proc.,' A, vol. 92, p. 555 (1916).

$$k[E] = \frac{[Q]}{C_0}, \tag{8A}$$

from which the value of the net change of electric field [E] may be calculated In method (C) a string electrometer, kindly lent by Prof Sir Ernest Rutherford, was used This had a sensitivity of about 30 to 60 divisions per volt, depending on the potential difference between the plates In this case formula (9) applies again directly if C_1 is taken as the capacity of the electrometer and connecting leads

Methods (A) and (B) were used at Aldershot, Helwan and Khartoum, while method (C) was used at Cambridge At Aldershot, Helwan and Khartoum aerial systems of large effective height and capacity were used as the exposed conductors, while at Cambridge, through the kindness of Prof Wilson, we were able to use the aerial system, consisting of an exposed elevated insulated sphere which he has used previously in his researches* on the electrical field of thunderstorms. In all three methods it was estimated that field changes down to about 0·1 volt per metre were measurable, and thus the measurements may be regarded as an extension of those made, at much shorter distances from thundercloud discharges, by Prof Wilson himself

Although measurements of the sign and magnitude of over 3,000 net changes of field associated with thundercloud discharges have been made, it is not proposed to consider here a detailed analysis of all the measurements, for the experience gained in the preliminary measurements has led us to hope that a slightly improved technique, with facilities for photographic registration, will give more reliable evidence for the cases of multiple discharges, which commonly occur, and which must be considered in a detailed analysis One result of the preliminary data is, however, quite definite, and will be discussed below under the sub-heading (*a*) Some specimen groups are given under sub-heading (*b*)

(*a*) *Relative Numbers of Positive and Negative Changes of Electric Field.*—To establish a convention as to sign, the earth's normal fine weather gradient will be taken as a positive field Such a field tends to send a current of positive electricity (the ordinary air-earth current) down an exposed conductor The destruction of a negative thundercloud moment will therefore produce a positive change of field and *vice versa* Thus on the destruction of a negative thundercloud moment the positive bound charge on an exposed conductor will be released and pass to earth down the earth lead. Thus the sign of the charge passing down an aerial is directly indicative of the field change

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* Wilson, 'Roy. Soc. Proc.,' *loc. cit.*

It has previously been found by Prof Wilson* that the rapid field changes associated with lightning flashes show a preponderance of positive changes over negative changes the ratio being about 1 56 to 1 When our measurements were begun at greater distances from the discharge channel than those at which Wilson's readings were made, there was found an opposite preponderance, negative field changes being 1 7 times† as frequent as positive changes The relative number of positive and negative changes of field observed at the various stations and by the various methods are summarised below in Table VIII

Table VIII

Station method	Negative change	Positive change	Ratio	Reported thunderstorms.
Aldershot (A)	536	395	1 36	Frequently within 20 km
Aldershot (B)	468	81	5 8	Mainly beyond 150 km
Helwan (A)‡	69	0	—	None within 500 km
Helwan (B)	102	1	102	None within 500 km
Cambridge (C)	304	199	1 53	Frequently within 50 km.
Khartoum (A)	598	46	13 0	Mainly about 250 km

After the preponderance of negative field changes had been found in the early experiments it was natural for us to consider what difference there could be between the conditions of our experiments and the conditions under which Prof Wilson's measurements, which indicated the opposite preponderance, were carried out The only difference that could be suggested was that of distance from the site of the discharge Prof Wilson's observations were usually made within the region of audible thunder at a distance under 25 km

Our measurements were made usually just outside the region of audible thunder mainly at a distance of the order of 100–200 km. We thus must conclude that the sign of the preponderant field changes reverses as the distance from the discharge is increased The point is discussed in greater detail below

(*b*) *Specimen Data of Semi-Permanent Field Change Observations* —It may be useful to summarise three specimen groups of data on net field changes, comprising (α) the summary of an afternoon's and of a whole day's electrometer observations at Aldershot, (β) the results of a single evening's electrometer observations at Helwan, and (γ) notes on results from Khartoum

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* 'Phil. Trans.,' *loc. cit*

† In a letter to 'Nature' (113, 1924, p. 237) this ratio was erroneously given as 400 to 1 The results obtained up to that date were vitiated by insufficient sampling and also a biassing flaw in the apparatus.

‡ Only observations quantitatively confirmed by method B are here shown.

(α) *Aldershot, June* 25, 1923 —Observations between 1540 and 1800 G M T showed 12 negative discharges, after which the electrometer bubble remained in its displaced position, and 4 positive discharges of this type Seven negative discharges occurred in which the bubble moved in the reverse direction after a stationary period which was just sensible, no positive discharges of this type were noted In 23 negative discharges the bubble immediately returned, approximately to its original zero, 8 positive discharges were of this character

Aldershot, July 7, 1923 Observations between 0845 and 1745 are shown in Table IX, which includes also the data for June 25 above

(β) *Helwan, January* 13, 1924 —The observations made simultaneously by methods "*a*" and "*b*" between 1900 and 1945 G M T, in which 68 net field changes, all of the same sign, were observed by both methods, are best summarised in fig 12, in which are plotted the computed field changes from the two methods

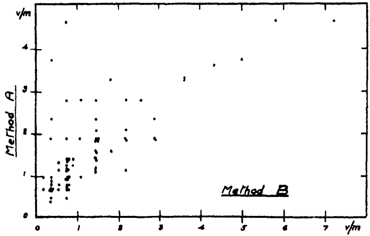

Fig 12

(γ) *Khartoum, April* 23, 1924 —Observations 2015 S T (1815 G M T) to 2430 S T (2230 G M T) Three lightning centres were visible at start, A to NNW, B to NW, C to NE, later a fourth centre D appeared in NNE No thunder was heard during this whole period. The centres were, therefore,

Table IX

Period.	Duration. Minutes	Semi permanent.				Double semi permanent.			Quick return.				Slow return			
		No	+ Mean δE	No	− Mean δE.	No	+ Mean δE.	− Mean δE.	No	+ Mean δE	No	− Mean δE	No	+ Mean δE.	No.	− Mean δE
June 25—																
1540–1800	50	4	43	12	283	—	—	—*	8	15	22	223	0		1	92
July 7—																
0845–0912	27	5	446	60	450	8	325 ←	— 612	0		12	71	0		3	600
0917–1002	45	33	84	58	384	31	329 ←	— 572(A)	3	31	51	173	0		14	434
1013–1045	33		—	26	1,011	1	138 ←	— 529	0		1	92	0			
1057–1116	17	0	—	19	1,450				2	23	27	46	2	103	2	35
1236–1249	13	2	517	1	46	1	115 —	→ 69								
1400–1416	16	10	34	18	423	2	46 —	→ 103	3	35	0		1	46		
1453–1500		1	46	2	150				1	23			0			
1718–1745	27	3	169	28	719			(B)					1	46		
Total ..		58	122 5	230	611	43	305	545	17	23	113	141	4	74	30	409

* In column " double semi-permanents " arrow runs from earlier to later component of discharge.
(A) Also 4 double negative discharges, viz., — 115, — 138, — 92 — 46 — 230 — 69, and — 460 — 230 — 600
(B) 1 double discharge, — 368 followed by — 115

probably beyond 30 km., but within 300 km. The number and mean magnitude of the net field changes observed to be associated with flashes from each of these centres, as reported by a second observer, were as undernoted, viz.:—

Centre A, 12 positive, mean field change 0·136 v/m, 86 negative 0·062 v/m
Centre B, 2 positive, mean field change 0·046 v/m, 10 negative 0·035 v/m
Centre C, 6 positive, mean field change 0·380 v/m, 181 negative 0·133 v/m
Centre D, 7 positive, mean field change 0·062 v/m, 40 negative 0·103 v/m

Totals observed, including a number of observations before correlation with sources was begun, 37 positives of mean 0·163 v/m, 444 negatives of 0·106 v/m. The most interesting features of the observations, however, were not the measurements of number and amplitude, but the visible characteristics in relation to the sign of the discharge. Centre C was higher in angular elevation than the others, presumably on account of greater proximity; this is supported by the magnitude of the field changes. Five out of the six positive field changes from C were seen to be the result of discharges from cloud to earth, and no other discharges to earth from this centre were seen. The sixth positive from C was of a magnitude (0·8 v/m) only twice equalled during the evening, once in a cloud to earth discharge from C, once in a discharge of doubtful type from A. The other discharges from C were diffused more or less symmetrical glows described at the time of observation as resembling Very lights. In the case of centres A and D the positive field changes were characterised by the markedly greater durations of the illumination from the visible lightning. This duration averaged some three seconds. In fact, once this relation had been noticed, the second observer, who was unable to see the oscillograph, was able in every case and without error to state the sign of the field change from the appearance of the flash. In the case of D, the elevation was too low to show the track of the discharges, but the positive field changes were characterised by discharges of greater brightness as well as of longer durations, and were believed to be cloud to earth discharges.

On the evening of the 24th three centres were observed; E gave 2 negatives of 0·14 v/m mean, F 44 of 0·21 v/m, G 12 of 0·36 v/m, while only one positive was observed during the whole evening, this was of 1·15 v/m, and originated in G, this flash being by far the brightest of the evening.

On the 25th four centres gave, H 36 negatives of 1·0 v/m, L 37 negatives of 2·6 v/m, M 22 of 2·0 v/m, N 1 of 0·14 v/m. H gave 2 positives, one of 1·8 v/m from a cloud to earth flash and one of 1·4 v/m type of flash unknown, M gave 6 positives, mean 2·2 v/m, four from cloud to earth flashes, and one reaching 3 2 v/m, an exceptionally brilliant flash whose path was not traced, but which was described as giving a "searchlight" effect

A watch was kept for evidence of "trigger action," but the results were scanty In one case C gave − 0 11 v/m followed instantly by + 0·8 v/m, and again − 0 11 v/m followed by + 0·16 v/m, this latter being a cloud-earth flash. Source A gave − 0 04 v/m followed by + 0·10 v/m

Source D gave a − 0 04 v/m followed by + 0 08 v/m, the latter a cloud-earth flash In another instance − 0 04 v/m from a C discharge was instantly followed by + 0 92 v/m from source A On one occasion discharges of D, C and A, the latter of + 0 04 v/m, followed in such rapid sequence that they appeared to result one from the other

This evidence seems consistently to show that a positive field change, *i e*, a net transfer of positive electricity down the aerial, indicating an increase of the normal gradient, is associated with a cloud to earth discharge, and that this type of discharge is characterised by long duration and great brilliancy Such discharges seem also to be preceded, in some cases at least, by a negative field change of smaller amount Negative field changes in general are smaller in magnitude, and are associated with brief diffuse glows, presumably upper air discharges

Further visual observations from the Tropics are of importance in this connection. It was first observed by us at Aden, and again in the Indian Ocean, that the centre of illumination in lightning flashes underwent a displacement in azimuth sufficient to be clearly distinguished by visual observation It chanced that on these occasions no determinations of the sign of the associated field changes could conveniently be made In the Khartoum observations, however, a watch was kept for this phenomenon It was found that, in the observations of April 23, almost all of the diffuse glows with which were associated negative field changes were displaced Eastward in azimuth within the duration of the glow, while at least six of the discharges associated with positive field changes were displaced Westward On a later evening, with storms to the Southward, sources of negative field changes were again displaced Eastward, while on two occasions with storms in the West no azimuthal displacement was observed

These observations suggest the hypothesis that these displacements are electro-dynamic in origin, and result from the action of the earth's magnetic field. If this hypothesis be accepted, it would follow that the direction of current flow in the discharges producing a negative field change is downward, while that in a discharge giving a positive field change is upward.

Summing up, there appears to be considerable evidence to show that the typical discharge in these storms consisted of (*a*) a downward discharge, in the upper air, of a positive charge, followed by (*b*) a downward discharge to earth of a negative charge

III —*The Meteorological Environment*

The general weather conditions prevailing during the measurements of series IV may be summarised in an extract from the Monthly Weather Report of the Meteorological Office for the year 1923, as follows —

> " A general deterioration occurred near the end of the month of August with severe gales even at some inland stations During the early part of September fair, warm and sunny weather prevailed generally in the south, and an improvement also took place in the north and west Towards the end of the second week, however, the tracks of depressions lay further to the south and unsettled weather became general with occasional gales and thunderstorms Toward the end of the month an anticyclone over France spread northward, giving warm but somewhat misty weather October was characterised mainly by unsettled, boisterous weather with south-westerly winds, often of gale force, frequent squalls and heavy rainfall The temperature was moderate There were, however, considerable bright periods, with the result that some parts of the country experienced an excess of sunshine as well as an excess of rain After a few mild days at the beginning of November the weather was cold . "

Pressure was below normal throughout these months, the mean isobars trending from W or W S W to E or E N E, while an almost uninterrupted succession of depressions crossed the British Isles, giving high winds, and precipitation considerably in excess of normal The British thunderstorms, the times of occurrence of which were reported as falling in the evening, have been examined in relation to the atmospheric disturbances received on each individual evening Such an examination is necessarily incomplete and one-sided, since it neglects the effects of continental thunderstorms which may be at much smaller distances than are storms reported from British stations Thus the Shetlands are approximately as far from the observing station as are Berlin, Marseilles and San Sebastian, so that the meteorology of much of Europe ought to be examined equally with the British reports. With the exception of one or two storms appearing in the French Daily Weather Report, however, only British storms have been considered

It is of interest, therefore, to note that in this limited sector, thunderstorms were reported on 25 of the 42 evenings of observation The relation to these storms of observed quasiperiodic disturbances of amplitude exceeding 0 15 v/m and net changes of field of apparent duration exceeding 0 03 seconds, may be briefly summarised Of 171 such changes of field observed during the whole period, only 15 occurred on evenings without reported thunder, 8 of the 12 occurring on one single evening (September 25) The remaining 7 discharges were distributed over five evenings Of 188 positive quasiperiodics of the large amplitude specified, 27 occurred on eight evenings without reported thunderstorms, 16 on one such evening, 6 on another Of 105 large negative quasiperiodics, 28 appeared on evenings of no reported thunderstorms, while of 242 large quasiperiodics of the Q ± type 67 appeared on such evenings Next to the apparent net changes of field, therefore, the large positive quasiperiodic atmospheric appears to be the most closely correlated with lightning within a few hundred kilometres

IV --*Discussion of Results*

As mentioned previously, it was not considered profitable, in our preliminary account of these experiments in 1923, to discuss the possible sources of atmospherics in the light of the data revealed by these experiments, and in the present paper it is proposed to remedy this omission to a certain extent But it must be stated at the outset that there are many points on which information is still lacking, as must necessarily be the case in a type of wireless propagation experiment in which the location of the transmitter is unknown We can therefore only outline in somewhat general terms the views to which we have been led.

It was evident, when the first wave-form oscillograms were seen, that the impulses were of quite different nature from ordinary wireless signals, the wave-forms of which (*e g*, from St Assise) were often visible for comparison on the oscillograph screen The maximum amplitudes, as is seen from the data in the tables, are often of the order of 0 1 volt per metre, which is more than a thousand times the field intensity of an ordinary commercial wireless signal. On the other hand, the mean duration of many atmospherics was found to be surprisingly long, *e.g.*, 2,000 microseconds, which may be compared with the time periods of the order of 1 to 60 microseconds which are in use commercially

Means for the determination of the sources of such disturbances are only now becoming available. Very strong experimental evidence has been adduced to show that lightning discharges produce atmospherics which are audible in short-wave receivers at distances over 1,000 km * and in some cases exceeding 2,000 km. The evidence here referred to is the close coincidence in place and time between sources of atmospherics located by direction finding and the occurrence of observed lightning The experiments of Baumler,† although the experimental conditions were not sufficiently rigorous to make the results absolutely conclusive, indicate that the time of incidence of 50 per cent of the atmospherics recorded in Germany along with European time signals agreed with the time of incidence of atmospherics recorded in America along with the same time signals Such experiments apart from the limitation mentioned, argue normal ranges of reception of atmospherics reaching 3,000 km These entirely independent methods of measurement thus assign minimum reception ranges of the same order

Direct visual observation sufficed to show that the net field changes measured in the course of the present work were indeed due to lightning at no great distance, certainly within a few hundred kilometres It was also established that such net changes were accompanied by the production in the oscillograph of images of the same type as those, frequently of much smaller amplitude, given by ordinary atmospherics There is, then, no room for doubt that we must look to thunderstorms, up to very considerable distances, as important sources of typical atmospherics, and reciprocally that the study of the wave-forms of atmospherics produced by thunderstorms will give us information relating to the temporal variation of the electric moment of the thundercloud during the flash Since atmospheric wave-forms known to originate in simultaneously observed lightning flashes showed only one complete main cycle, of fairly long duration, it was clear that lightning is not, in general, as has usually been assumed, freely oscillatory This result is in agreement with the results of the experimental study of the effects of atmospherics on wireless receivers of different frequency, from which there is no evidence of specially marked response at any particular wave-length.

It is therefore of interest to consider at the outset what electromagnetic effects are to be expected by the discharge of a thundercloud with characteristics such as may be deduced from Prof Wilson's work on the electrostatic fields of thunderstorms Let us consider an ideal thundercloud of quantity Q the centre of which is at a height h above the ground (see fig 13)

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* Watson Watt, 'J. Roy Aero. Soc.,' vol. 29, p. 62 (1925).

† Baumler, 'Jahrbuch der drahtl. Tel. u. Tel.,' vol. 22, p. 2 (1923).

Since the ground may be considered as approximating to a perfect conductor, the electric moment of the thundercloud system will be $2hQ$. At any point P

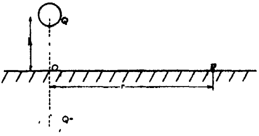

Fig 13

on the ground, distant r from O, where $r >> h$, the vertical electrical field E at any time will, if three-dimensional divergence of energy be assumed, be given by*

$$\mathrm{E} = \frac{\mathrm{M}}{r^3} + \frac{\frac{d\mathrm{M}}{dt}}{cr^2} + \frac{\frac{d^2\mathrm{M}}{dt^2}}{c^2r}, \tag{13}$$

where the values of the quantities involving M are the retarded values obtaining at a time $(t - r/c)$, c being the velocity of electromagnetic radiation. We may for convenience, refer to the three terms on the right hand side of (13) as the electrostatic, induction and radiation terms respectively. From this expression it is clear that, at short distances from the discharge, the electrostatic term is the important one, but that at more distant points, the radiation field predominates The critical distance at which these terms are equal in magnitude depends on the nature of the discharge

It is clear that the initial and final values of the induction and radiation terms will be zero, so that the net change of the electric field will indicate the change of the electric thundercloud moment brought about by the discharge Measurements of such net changes have been made by Prof Wilson at short distances and by ourselves at greater distances from lightning discharges, and the results taken together indicate that many thunderclouds cannot be regarded as possessing a charge of one sign only, since the sign of the electric field change is not the same at all distances. Further reference will be made to this point below. Meanwhile, we shall consider an electric moment of the simple structure depicted in fig. 13.

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* *Cf.* Pidduck, 'A Treatise on Electricity,' p. 446.

It seems fairly clear from the atmospheric wave forms observed that the main discharge causing the disturbance is not freely oscillatory, though the ripples frequently observed are possibly due to minor oscillations The electrical system of the thundercloud and the discharge channel possesses capacity, inductance, and resistance, and, if sufficiently accurate estimates of these quantities were available we might calculate approximately the quantity $f(t)$ But much more information is required before this can be done satisfactorily, since it is most likely that the resistance varies considerably during the discharge *

Let us assume, however, as a working hypothesis, that the electric moment of the thundercloud remains throughout the discharge of the same sign, the discharge therefore being aperiodic The current in the discharge channel (which determines the magnitude of the induction term in (13)) will thus be unidirectional The rate of change of current (which determines the magnitude of the radiation term in (13)) will, however, change sign so that the radiation wave-form will consist of both a positive and a negative field change A physical interpretation of this is that we may regard one impulse as produced by the acceleration of the moving electric charge and the other as due to the retardation of the charge Now a typical atmospheric wave-form which we have observed in association with lightning at no great distance is exactly of this character, and we are therefore led to examine more closely the interpretation of atmospheric wave forms as radiation fields produced by distant aperiodic discharges In particular we may inquire what type and magnitude of thundercloud moment change would produce radiation fields, at distances of 3,000 km, such as we have observed

If we neglect, as we may at large distances the electrostatic and induction terms in comparison with the radiation term we have from (13) the change of moment [M] during the period of the atmospheric

$$[M] = c^2 r \iint \mathrm{E}\,(dt)^2 \tag{14}$$

But for such low frequency changes as we are considering the atmospheric ionized layer and the earth act as good conductors, and so make the diminution of electric force with increase of distance slower than that assumed in the formula In fact, for two-dimensional divergence of energy between two good conductors the electric force would tend to vary as $1/\sqrt{r}$ and not as $1/r$, as was first pointed out and experimentally supported by Eccles † But since the discharge does not take place between the ionized layer and the ground we may not assume such a law of electric force attenuation for all distances from the source. We may, however, assume that a fair approximation to two-dimensional divergence takes place for distances which are greater than a certain distance r_0 which is a small multiple of the height of the layer. In accordance with recent estimates* of the height of the ionized layer, we may reasonably take r_0 as 300 km., in which case the relation (14) must be altered to

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* Watt and Appleton, *loc. cit.*, p 98.

† Eccles, 'Wireless Telegraphy and Telephony,' London, p 153 (1918)

$$[M] = c^2 \sqrt{r_0 r} \iint E\,(dt)^2 \qquad (15)$$

To find the change of electric moment necessary to cause these impulses we must therefore integrate E twice with respect to t. Such integrations have been carried out graphically for the atmospheric which, from the examination referred to on p. 662 is believed to be typical of lightning at 300 km., and the results are illustrated in fig. 14, where graphs representing quantities pro-

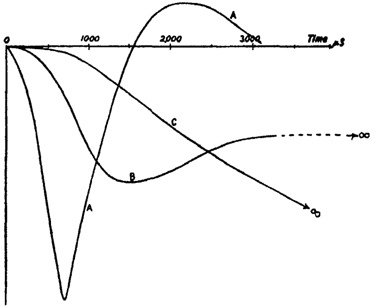

Fig. 14.

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* Appleton and Barnett, 'Nature,' London (1925); Round, Eckersley, Tremellen and Lunnon, London, 'Jour. I.E.E.,' vol. 63, p. 933 (1925).

portional, on widely different scales, to d^2M/dt^2 dM/dt, and M are shown at A, B and C, respectively

It is seen that the curve of dM/dt is one side of the axis representing a unidirectional current discharge, while the change in M is in one direction only It is interesting to note that both the graphs representing dM/dt and M strongly suggest that the discharge continues after the radiation field becomes too small to be measured on the oscillograph This is possible if the continuation of the electric moment change were either very slow or linear

The change of moment [M] which occurs during the period in which the radiation field is of measurable amount can be computed from (14) and (15) The change of moment can also be computed from the net change of field using the first term of (13)

This has been done for the field changes found to be characteristic of distances of 100 300 and 600 km from the source and the results are shown in Table X

Table X

r	Moment calculated from	
	Net change	Radiation field
100 km *	$>2\ 0 \times 10^{16}$	$>1\ 1 \times 10^{17}$
300	$2\ 7 \times 10^{17}$	$1\ 9 \times 10^{17}$
600	$2\ 2 \times 10^{17}$	$2\ 3 \times 10^{17}$

* Deflections off scale lower limit only deducible

This very satisfactory agreement between the two methods of computation and with Prof Wilson s estimate (3×10^{16} e s u , itself a lower limit) justifies the further use of the field strength distance law of (15) to determine the probable radiation field at 3 000 km The resulting value 0 06 v/m, is, in fact the most frequently observed radiation field strength in the present series Thus it is clearly established (*a*) that the destruction of thunderstorm moment necessary to produce the electrostatic and "radiation" field changes measured at known distances up to 600 km from the source is of the same order as that measured by Prof Wilson and (*b*) that such a destruction of moment is sufficient to produce at distances of 3 000 km from the source radiation fields of the magnitude most frequently measured in our observations, and that the fields from such sources will be measurable, by the methods described, at distances over 10 000 km *

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* We are particularly indebted to Dr G C Simpson for most valuable suggestions in connection with this part of the discussion.

We now proceed to discuss the results of the measurements on semi permanent field changes It has been shown that there is a preponderance of sign, in that negative changes of field are at least 1 7 times as frequent as positive changes also that this preponderance is opposite in sign to that found by Prof Wilson who in measurements on 864 discharges found positive discharges 1 56 times as frequent as negative discharges It has been pointed out above that the only difference between Prof Wilson s measurements and ours has been the difference in the distances of the observing station from the discharge and thus we conclude that certain discharges must take place which produce a positive change of field near the discharge and a negative change at greater distances Considerable support for this view is to be found in Prof Wilson's own measurements where it may be seen that the preponderance of sign found by him is not the same at all distances For example, in the readings made at distances less than 5 km the preponderance increases to a ratio of 4 to 1, whereas at greater distance (*e g* 5-30 km) the ratio is only 1 5 to 1

Using Prof Wilson s measurements alone it is natural to associate the preponderance of positive over negative field changes as indicating that thunder cloud discharges are more often the discharge of clouds of negative moment than clouds of positive moment and in this way the results might be interpreted as a confirmation of Simpson's theory of thunderstorms according to which the air in a thundercloud is charged with negative electricity, the corresponding positive electricity having been brought to the ground in the form of rain But when our observations are taken into account such a view hardly seems tenable Since the sign of the field change is most frequently positive at short distances and most frequently negative at greater distances we must conclude that a thundercloud is frequently if not always bi polar and, to account for the sign of the field changes we must assume that a frequently occurring type of thundercloud is one with the positive charge uppermost and the negative charge underneath the resultant moment being positive This disposition of the electric charges is opposite to that involved in Simpson's theory of heat thunderstorms according to which the negatively charged air would be situated above the positively charged water drops

It ought, however, to be mentioned that Simpson* has pointed out that the breaking of drops is not the only way in which electricity is produced in thunderstorms, and that the impact of ice particles (*e g*, in hail storms) produces this effect Simpson has shown that, when drops break, the air acquires a negative charge but that when ice separates the air becomes positively charged Thus it seems possible that bi polar thunder clouds of both signs might occur

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* 'Phil. Mag.,' London, 30, 1 (1915); Nature,' London, 112, 727 (1923).

Let us consider the effect of a bi polar cloud of the type suggested by the field change observations Let h be the height of the negative charge ($-$ Q) and H the height of the positive charge (assumed for simplicity to be $+$ Q) as in fig 15

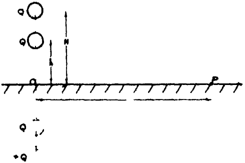

Fig 15

The vertical electric force E due to such a system at a distance r allowing for the image effect of the ground is given by

$$E = \frac{2QH}{r^3\left(1+\frac{H^2}{r^2}\right)^{3/2}} - \frac{2Qh}{r^3\left(1+\frac{h^2}{r^2}\right)^{3/2}}$$

$$= \frac{2Q}{r^3}\left\{\frac{H}{\left(1+\frac{H^2}{r^2}\right)^{3/2}} - \frac{h}{\left(1+\frac{h^2}{r^2}\right)^{3/2}}\right\} \tag{14}$$

The electric force becomes zero at a certain critical distance r_e For values of r less than this the electric field is negative for distances greater than r_e it is positive The value of r_e is given by

$$\frac{H^2}{\left(1+\frac{H^2}{r_e^2}\right)^3} = \frac{h^2}{\left(1+\frac{h^2}{r_e^2}\right)^3} \tag{15}$$

or if

$$a = \frac{H^2}{r_e^2} \quad \text{and} \quad b = \frac{h^2}{r_e^2}$$

by

$$\frac{a}{(1+a)^3} = \frac{b}{(1+b)^3} \tag{15A}$$

It is clear that if data were available for two of the three quantities H, h, and r_c, the other quantity could be calculated A further reference to such a calculation is made below.

We now turn to discuss some evidence which appears strongly confirmatory of the conclusions stated above with regard to the disposition of the electric charges in many thunderclouds As has been previously mentioned, no attempt has been made to analyse the net-change of field determinations beyond establishing the preponderance of negative field changes when measurements are made at distant points from the discharge channels But two sets of observations having special bearing on the matter discussed immediately above may be mentioned The Khartoum observations cited in II (*b*) (γ), appear to indicate that the bottom of the thundercloud was negatively charged since the discharge of the bottom of the cloud to ground resulted in the destruction of a negative moment They also indicate that when the discharge took place in or above the cloud a positive moment was destroyed Thus the evidence taken as a whole indicates a thunderstorm mechanism which elevates the positive above the negative charge

It has been previously shown that, in the case of a bi-polar thundercloud the field should be zero at a certain critical distance r_c, and many of the sets of readings were examined to see if an estimate of this quantity could be obtained. In the majority of cases no doubt the simultaneous occurrence of several neighbouring storms makes it impossible to pick out the discharges of any one storm But on August 1, 1925, at 4 45 p m (G.M T) measurements were made at Potters Bar on the discharges of what appeared to be a single thundercloud. Here it was found that as the storm approached the changes of field were first small and negative These were followed by positive field changes which increased in magnitude and then decreased, finally changing to small negative changes again. There can be little doubt that here we had an example of a bi-polar cloud, the electric field of which reversed at a certain critical distance, which, from intervals between the crashes as heard in a wireless set and the thunder, appeared to be about 8–10 kilometres

The results discussed above obviously have a bearing on Prof. Wilson's theory of the maintenance of the earth's charge. According to this theory the earth's negative charge is maintained (in spite of the normal fine weather air-earth current of 1,000 amperes which tends to neutralise it) by the action of thunderclouds which send intense negative ionization currents to the ground. It has been shown above that a frequently occurring type of thundercloud is that with the positive charge uppermost and negative charge underneath, which will act as a large source of electromotive force tending to send positive electricity to the upper conducting layer and negative to the ground. Such transport of electricity is of the type required to account for the maintenance of the earth's charge according to this theory.

During the wave form observations it was frequently found that due to the presence of neighbouring thunderclouds or shower clouds an appreciable current was flowing in the aerial circuit producing an electromotive force across the resistance ρ (see fig 3) of sufficient magnitude to move the oscillograph spot off the screen. It was usually possible to bring the spot back to the zero position with the aid of the potentiometer P_1 (see fig 3) but very often the potential across ρ could not be neutralized with the potentiometer battery of 20 volts, normally used. It seems fairly clear that the phenomenon was due to the intense ionization currents which flow to the ground because of the brush discharges which are produced at the surface of the aerial by intense potential gradients due to charged clouds. The order of magnitude of the field at the surface of the aerial wire may be estimated approximately as follows. Let us consider an aerial of capacity C_0 of such a shape that the capacity is mainly due to the horizontal portion which is a wire of radius r length l and average height h. Then if dV/dh is the undisturbed potential gradient the charge of unit length q of the wire will be given approximately by the product of the capacity per unit length (C_0/l) and the undisturbed potential at height h $(h\ dV/dh)$. Thus

$$q = \frac{C_0}{l}\ h\ \frac{dV}{dh}$$

Now as a rough approximation we may consider this charge as uniformly distributed over the surface of the wire so that the charge per unit area σ is given by

$$\sigma = \frac{C_0}{l}\ h\ \frac{dV}{dh}\ \frac{1}{2\pi r}$$

The electric field E at the surface is thus given by

$$E = \frac{C_0}{l}\frac{4\pi h}{2\pi r}\frac{dV}{dh} = K\frac{dV}{dh} \tag{16}$$

The constant K therefore represents the number of times the normal earth's field on flat ground is increased at the surface of the aerial. In our case we had $C_0 = 0.0027$ mfd $= 2\,500$ cms and $h = 500$ metres $l = 15$ metres $r = 0.2$ cm

Therefore

$$K = \frac{2{,}500 \times 2 \times 1{,}500}{50{,}000 \times 0\ 2} = 800$$

We thus see that on a normal day, when the atmospheric gradient is 100 volts per metre, the gradient at the surface of the aerial wire is 80,000 volts per metre,* which would tend to produce brushing It is then evident that if the vertical potential gradient is increased in numerical magnitude due to the presence of charged clouds vigorous brush-discharges may be expected to occur on a wireless aerial resulting in comparatively large currents in the aerial system In this way currents of 40 microamperes were very often measured. Both positive and negative currents down the aerial were observed, the change of sign often taking place within a minute or so

Thanks are due to the Department of Scientific and Industrial Research, which, on the advice of its Radio Research Board, provided facilities for the work described, and accorded permission to publish the results We are indebted to the Atmospherics Committee of the Radio Research Board, and to two of its members in particular, Prof C T R. Wilson and Dr G C Simpson, for their interest and advice at all stages of the work We gratefully recognise how much we are indebted to Prof. Wilson's published work on 'Atmospheric Electricity' for guidance in the interpretation of the experimental results

Appendix I

The triode circuit shown in fig 5, and briefly described on pp 624–5, is of intrinsic interest as an example of a non-linear assembly apart from its present use in the production of the special form of oscillograph time-base utilised in these experiments As it was necessary to know the factors controlling the characteristics (*e g*, voltage amplitude, time of "backstroke," etc) of this base, a separate investigation was made to determine the factors influencing the periodic grid-voltage changes in this system In this investigation (in which we had the valuable assistance of Mr F A Bannister, of the Cavendish Laboratory) certain facts emerged which have enabled us to construct what appears to be an adequate account of the working of the oscillator

The circuit of fig 5 is redrawn in fig A, where the diode, for simplicity in explanation, has been replaced by a simple resistance R

It is seen that, apart from the capacity C and resistance R the circuit is a simple triode oscillator assembly with electromagnetic reaction. If the coupling

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* The action of a possible local space charge is here neglected.

M between L_1 and L is of the correct sense and magnitude (depending on C_1 L_1 r and the triode parameters) high frequency oscillations will start in the

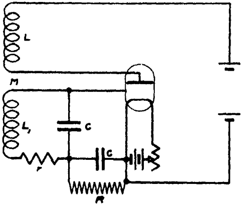

FIG A.

circuit L_1C_1 in the usual way Such oscillations are still possible in the presence of C since its reactance is small at such high frequencies But if the resistance R is sufficiently large to effect a partial insulation of the grid as in the present experiments the effect of the grid current on the mean grid potential must be considered

Let us suppose that due to the self excited oscillation a potential difference E exists at any instant across the condenser C_1 Then it may be shown* that the grid potential v (between grid and filament) is given by the relation

$$\frac{dv}{dt} + \left(\frac{1}{RC} + \frac{\alpha}{C}\right) v + \frac{\beta v^2}{C} = \frac{dE}{dt} \qquad \text{(A)}$$

where the non linear relation between the grid current i and the grid potential v is written as a first approximation

$$i = \alpha v + \beta v^2 \qquad \text{(B)}$$

In the present case E is oscillatory so that

$$E = a \sin \omega t$$

An approximate solution of (A) in this case is

$$v = -\frac{\beta}{2q}\left(\frac{a^2\omega^2}{\omega^2 + \frac{q^2}{C^2}}\right) + \frac{a\omega}{\sqrt{\omega^2 + \frac{q^2}{C^2}}} \cos(\omega t - \phi)$$

$$+ \text{ term of angular frequency } 2\omega \qquad \text{(C)}$$

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* Appleton and Taylor 'Proc. Inst Rad. Eng vol 12, No. 3, p 294 (June, 1924)

where

$$q = \frac{1}{R} + \alpha$$

We thus see that, as a result of the partial insulation of the grid, the mean grid potential $\bar{v}$ finally assumes a negative value* (given by the first term in the expression for v), determined by the amplitude of the oscillation, the resistance R and the grid current characteristics

But in a self excited oscillator, such as we are considering, the amplitude of the oscillation is determined by the mean grid potential so that as $\bar{v}$ becomes more negative the value of (a) alters The solution (C) is therefore not generally applicable The inadequate mathematics, due to the intractable nature of the general non linear equations describing the whole phenomenon, may, however, be supplemented by experimental results The relation between the amplitude of oscillation and mean grid potential has therefore been determined in an experiment in which the mean grid potential was varied continuously by means of a potentiometer To determine the amplitude of oscillation a detecting coil in series with a crystal detector and sensitive galvanometer was weakly coupled to the coil L_1

The relation between the galvanometer reading (which is proportional to the square of the oscillatory current) and the mean grid potential is shown in fig B together with the ordinary grid potential/anode-current characteristic of the triode

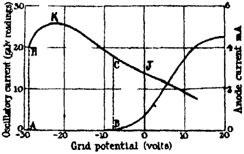

Fig B

It will be seen that when the mean grid potential is zero an oscillatory amplitude indicated by the point J obtains, but that as the mean grid potential becomes negative the oscillatory amplitude passes through the values indicated by C, K and H When the mean grid potential reaches the value of − 29 volts the oscillation is no longer maintained and the grid potential must now be reduced to − 7·8 volts before the oscillation starts again We thus get an oscillation-hysteresis cycle, and it is on this that the peculiar action of the oscillator depends Let us now consider what happens when the cycle of grid potential is brought about, not by means of a potentiometer but by the action of grid current on a partially insulated grid, in the manner described above When the oscillation starts the grid becomes rapidly negative If the resistance R is not too high a kind of equilibrium may be finally attained so that the mean grid potential remains fixed at a negative value For example, to get maximum oscillatory current from this particular triode the value of R could be adjusted so that the grid potential reached − 22 volts, in which case the oscillatory current would be represented by the point K.* Other things being the same, this equilibrium mean negative grid potential will be numerically greater the greater the value of R But if, as in our experiments, R is made very large, the mean grid potential may proceed to the extreme value of − 29 volts and still not have reached an equilibrium value, in which case, due to the inductance in the circuit, the mean grid potential will momentarily become more negative than − 29 volts and the oscillation is suddenly quenched The grid condenser now charged to − 29 volts discharges through the resistance R in the usual exponential fashion, the rate of discharge being determined by the magnitude of CR until the region of finite anode current is again reached, when, at − 7·8 volts, the oscillation begins again and the cycle is repeated. Thus while the oscillatory amplitude undergoes changes indicated by the curve BC, K, HA, the mean grid potential rapidly changes from B to A. During the return half of the cycle no oscillation exists while the grid potential alters slowly from value A to value B † When used for the production of a unidirectional time-base the rapid grid voltage change from B to A produces the invisible transit of the oscillograph spot from right to left, while the slower change from A to B controls the left to right transit during which wave-form observations are made.

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* α and β are in normal cases both positive.

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* For further details on this point *vide* Appleton and Thompson, 'Journ. I.E.E.,' vol. 62, No. 326, p. 183, February, 1924.

† That this view of the action of the oscillator is the correct one was verified by discharging the grid condenser through a ballistic galvanometer immediately after the cessation of a train of high frequency oscillations. From the quantity of electricity discharged the voltage of the condenser was estimated to be about equal to the grid potential necessary for stopping oscillations. In this experiment the grid condenser and leak were both made very large so that the time between two trains of oscillations was about 2 minutes

We thus see that the amplitude of the grid potential change AB available for use on the oscillograph is the difference between the limiting grid potentials for the starting and stopping of oscillations.* This difference increases with increase of retroaction and anode potential. We should therefore be able to control the length of the time-base by means of these variables. This has been found to be possible. The above explanation also suggests that the time of the charging of the grid condenser should be smaller the larger the frequency of the circuit, the smaller the capacity C and the larger the grid current. This has been confirmed in a general way, for the shortest time of the right to left transit of the oscillograph spot is always obtained when the capacities C_1 and C are as small as possible and the triode filament is bright. To make the discharge of the condenser uniform and not exponential a saturated diode is used, as previously mentioned, in place of the resistance R. The time of the left to right transit of the spot is usually controlled by varying the emission of the diode rather than by varying the condenser C which, for reasons given above, is kept at a low value.

It is recognised that there is, however, a limit to the smallness of C, for with very small values of C its large reactance precludes effective grid relay action and self-oscillation in the circuit becomes impossible.

Summary

The experiments on atmospheric wave-forms recorded in preceding papers have been supplemented by observations on the net changes of the earth's electric field, resulting from lightning discharges. These observations have been made at Aldershot, Cambridge, Helwan and Khartoum, and show that, at distances greater than 50 km from the discharge channel, negative changes of field are at least 1.7 times as frequent as are positive changes. Since the field-changes at such distances may be taken as indicative of the sign of the thundercloud moment destroyed by the flash, it is concluded that lightning flashes resulting in the destruction of positive electric moments are at least 1.7 times as frequent as are those of opposite character.

2. A satisfactory reconciliation with Prof. Wilson's determination of the electric field changes produced by lightning discharges within 25 km, in which an opposite preponderance of sign was obtained, is possible if thunderclouds are assumed to be bi-polar. Other evidence of such bi-polarity is cited.

3. It is shown that a frequently occurring type of thunderstorm mechanism is one which elevates the positive charge above the negative. This type of

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* *Cf.* Appleton and Thompson, *loc. cit.*

thundercloud polarity is that required by Prof. Wilson's theory of the maintenance of the earth's negative charge

4 Lightning discharges are shown to be capable of producing radiation fields similar in wave-form and magnitude to those of atmospherics of distant origin.

5. An Appendix deals with the theory of the linear time-base used in the observations on wave-forms

The Scattering of Alpha Particles through Small Angles

By D. C Rose, M Sc , 1851 Exhibition Scholar, Queen's University,
Kingston, Canada.

(Communicated by Sir E Rutherford, O M., Pres. R S —Received May 20, 1926)

The single scattering of alpha particles has been used for some time with considerable success to determine the properties of the electric field surrounding the nucleus of atoms, and also many of the properties of the atom itself An account is given in this paper of experiments on the scattering of alpha particles through small angles by thin gold foils It was hoped that these observations would give some information as to the nature of the electric field at some distance from the nucleus, and what effect the inner K shell of electrons has on it

In 1911, Rutherford* defined " single " scattering and developed the laws of single scattering based on an inverse square law for the field surrounding the nucleus. Later Darwin† extended this theory so that it could be applied to light atoms. In 1913 Geiger and Marsden‡ performed elaborate experiments on the scattering of alpha particles by metallic foils in order to test this theory of atomic structure. They observed the scattering of alpha particles of about 4 cms. range by gold foils over angles between 5 and 150 degrees It may be calculated that these angles represent distances of approach of the alpha particles to the gold nucleus between $4\ 6 \times 10^{-13}$ and $5\ 1 \times 10^{-11}$ cm Their results show that over this large range the law of inverse squares applies at least approximately In 1920 Chadwick[*] further confirmed the theory by measuring the atomic number of platinum, silver and copper by scattering Further experiments by Rutherford[†] Chadwick and Bieler[‡] and Rutherford and Chadwick[§] on the scattering of alpha particles by gases and light atoms show that the law of inverse squares breaks down when the alpha particle comes very close to or penetrates the nucleus From results of these experiments however important properties of the nucleus have been derived

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* 'Phil. Mag.,' vol 21, p. 669 (1911).

† 'Phil. Mag.,' vol. 27, p. 499 (1914).

‡ 'Phil. Mag ,' vol. 25, p. 604 (1913)

In this experiment we are concerned only with distant interactions between alpha particles and nuclei If an alpha particle is projected on to a thin foil, Rutherford[†] has shown that the probability of a deflection through an angle between ϕ and $\phi + d\phi$ is

$$\frac{\pi b^2 nt}{4} \cot\frac{\phi}{2} \operatorname{cosec}^2 \frac{\phi}{2}\, d\phi \tag{1}$$

where

$$\cot\frac{\phi}{2} = \frac{2p}{b} \qquad \text{and} \qquad b = \frac{2NeE}{mV^2}, \tag{2}$$

and p = distance from the original line of motion of the alpha particle to the nucleus

N = atomic number

e = electronic charge

E = the charge on the alpha particle

m = the mass of the alpha particle

V = the velocity of the alpha particle

n = the number of atoms per cubic centimetre in the scattering foil.

t = the thickness of the scattering foil

If we put Q equal to the number of alpha particles per minute incident on the scattering foil and y equal to the number per minute deflected through angles between ϕ_1 and ϕ_2, then on integrating we get

$$y = \frac{Q\pi b^2 nt}{4}\left(\cot^2\frac{\phi_1}{2} - \cot^2\frac{\phi_2}{2}\right) \tag{3}$$

If the field is to be investigated at relatively great distances from the nucleus, equation (2) shows that the angles must be small The radius of the K shell of electrons for gold, according to Bohr's atomic model, and data on the

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[*] 'Phil Mag, vol 40, p 734 (1920).

[†] 'Phil Mag,' vol. 37, p 537 (1919)

[‡] 'Phil. Mag,' vol 42, p. 923 (1921).

[§] 'Phil. Mag.,' vol. 50, p. 889 (1925)

K absorption limit, is $0{\cdot}69 \times 10^{-10}$ cm A calculation based on the above theory shows that an alpha particle from polonium, whose nearest distance of approach to the nucleus is this distance, would be deflected through an angle of 3 78 degrees Consequently, it was decided to attempt to measure the number of particles scattered through angles varying from one degree to eight For these small angles cot $\phi/2$ may be put equal to $2/\phi$ and equation (3) becomes

$$y = \mathrm{Q}\pi b^2 nt\left(\frac{\phi_2^{\,2} - \phi_1^{\,2}}{\phi_2^{\,2}\phi_1^{\,2}}\right). \tag{4}$$

If all the particles scattered between angles ϕ_1 and ϕ_2 are counted, that is, counting all those through an annular ring of inner radius d_1 and outer radius d_2, so that $\frac{d_1}{s} = \phi_1$ and $\frac{d_2}{s} = \phi_2$, where s equals the distance from the scattering material to the annular ring, see fig 1, then

$$y = \mathrm{Q}\pi b^2 nts^2\left(\frac{d_2^{\,2} - d_1^{\,2}}{d_2^{\,2}d_1^{\,2}}\right) \tag{5}$$

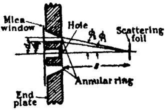

FIG 1.

This may be tested in two ways, first in the form

$$y = \mathrm{K}_1 s^2 \qquad \text{or} \qquad y = \frac{\mathrm{K}}{\phi^2}, \tag{6}$$

where ϕ is the average angle. This is quite accurate when $d_2 - d_1$ is considerably smaller than d_1 Secondly, the constant K may be evaluated from $\mathrm{Q}\pi b^2 nt\left(\frac{d_2^{\,2} - d_1^{\,2}}{d_2^{\,2}d_1^{\,2}}\right)$, which involves the dimensions of the apparatus, the size of the source, and the nature and thickness of the scattering foil.

By means of these relations it was hoped to investigate the nature of the nuclear field at distances from the nucleus from about Geiger and Marsden's outer limit to well beyond the K shell of electrons In order to use these relations, however, the scattering foil must be so thin that single scattering only is effective, that is, that the probability of a particle undergoing two or more atomic interactions, such that the deflections make up the angle under observation, is negligibly small. If the foil is thicker, so that the deflection of the particle is the resultant of a small number of atomic encounters ("plural scattering"), or if it is so thick that the deflection is the resultant of a very large number of atomic encounters ("multiple scattering"), different relations hold These problems have been discussed along lines based on earlier theories of atomic structure by Thomson,[*] Rutherford[†] and Darwin [‡] Later, papers by Jeans,[§] Mayer,[||] Geiger,[¶] Bothe,[**] and Wentzel[††] seem to indicate that for multiple scattering at small angles the scattering relation is similar to Gauss's error law, while at regions between multiple scattering and single scattering the relations worked out by Wentzel for beta rays seem to fit best He considers those which undergo no deflection, a deflection by one encounter, a deflection by two encounters, etc, separately, and totals them together for the final scattering function Wentzel also worked out a criterion for single scattering He showed that one can be sure of single scattering when $\phi \gg 4\omega$, where ω is the angle of single scattering corresponding to

$$p = \sqrt{\frac{2}{\pi n t}}, \tag{7}$$

p and ω being connected as in equation (2). This criterion is rather indefinite when one is concerned with regions where plural scattering is just noticeable The results of these experiments will be seen to give further information on this point

Apparatus and Method of Experiment.

A plan of the apparatus is shown in fig. 2. A source S of radio-active material was deposited on the end of a nickel or platinum wire about 0·8 mm in diameter. Just in front of S is an aperture A over which a mica window M of known stopping power may be placed to reduce the velocity of the alpha-particles A brass tube T was placed between apertures A and B to prevent particles scattered from the walls, etc, from getting into the counter without several deflections through large angles. This prevents stray particles from affecting the results The aperture B defines the beam of alpha particles used in the experiment. The diameter of A was 0 0828 cm and of B, 0 0853 cm This arrangement allows a slightly divergent beam of alpha rays to strike the scattering foil Jeans (*loc cit*) has shown that no correction for the angular divergence of the incident beam is necessary in the scattering relation provided the angles through which the scattering was measured were considerably larger than the outer limit of the divergence of the incident beam The smallest angle through which scattering was observed was 1 2 degrees and the apertures limited the divergence of the incident beam to about half a degree Another aperture C was placed in front of B of such size that it stopped the alpha-particles scattered from the edge of B just letting the main beam through The scattering foil F was hung in front of C in such a way that it could be lifted off by a hook The apertures source holder and scattering foil were held in place with adjusting screws so that they could be accurately lined up with the hole in the centre of the end plate E These screws fastened them to a slide which could be moved along a rigid square brass rod The whole apparatus was enclosed in a large brass tube so that it could be evacuated In the end plate E was cut an annular ring, with the above mentioned hole in its centre This was covered on the outside with a piece of mica fixed on with soft wax to make an airtight seal The alpha particles were counted by a Geiger electrical counter, placed as shown The mica window (about 2 cms stopping power) separated the counter from the rest of the apparatus Later some of the results were checked by the scintillation method in which case the counter and the mica window were replaced by a zinc sulphide screen.

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[*] 'Proc Camb Phil. Soc.,' vol 40 (1910).

[†] 'Phil. Mag,' vol. 21, p. 669 (1911).

[‡] 'Phil Mag.,' vol. 23, p. 901 (1912)

[§] 'Roy. Soc. Proc,' A, vol 102, p. 437 (1923).

[||] 'Ann. Physik,' vol. 41, p. 931 (1913).

[¶] 'Roy Soc. Proc,' A, vol. 83, p. 492 (1910), and vol. 86, p. 235 (1912)

[**] 'Z. f. Physik,' vol. 4, p 300 (1921).

[††] 'Ann. der Phys.,' vol. 69, p. 335 (1922)

The alpha-particles from S which get through C are scattered by the foil F Those scattered through angles between ϕ_1 and ϕ_2 as shown in fig 1, will enter the annular ring and be recorded The mean diameter of the annular ring was 0 596 cm, and its width (the difference $d_2 - d_1$) was 0 0175 cm The apparatus was of such size that the angle ϕ could be varied from about 1 to 8 degrees by moving the slide along the brass rod, to or from the end plate This was accomplished while the apparatus was evacuated by means of a stopcock windlass (not shown) at each end of the apparatus. Another stopcock windlass (not shown) worked the hook which lifted off the scattering foil This hook served a further purpose in that it could be let down between the aperture B and the tube T so that the beam of alpha rays was totally cut off and the effect of any stray particles detected None were found The distance from the scattering foil to the annular ring could be measured accurately by a calibrated scale on a brass rod, fig 2, one end of which was fastened to the slide The other end went out through a small brass tube in the end of the apparatus, as shown. A glass tube closed at the outer end was waxed over the small brass tube so that the position of the scale could be read opposite a mark at the end of the brass tube

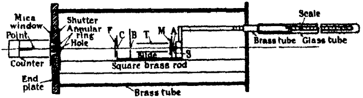

Fig 2

In front of the ring and hole was a shutter in the form of a wheel which covered them both The wheel could be turned while the apparatus was evacuated by means of a conical brass joint in the end plate, and had various apertures cut in it so that the entrance into the counter was in one of the following forms —

(1) Annular ring only
(2) Hole in centre only
(3) No opening at all
(4) Half of the annular ring, cut off vertically.
(5) Half of the annular ring, cut off horizontally

(1) was used for counting the scattered particles, (2) for the direct beam, (3) for finding the natural effect of the counter, (4) and (5) to check the alignment of the apertures Two plate glass windows in the side of the large brass tube made it possible to observe the setting of the shutter and the manipulation of the hook which removed the foil.

By drawing the slide back some distance from the counter end, and attaching a source of polonium in front of the foil F, the end plate could be uniformly bombarded with alpha-rays. By counting first through the annular ring and then through the hole and comparing the result with the ratio of the areas of the two as measured by a travelling microscope, the action of the counter over the whole annular ring could be tested. Great difficulty was experienced in getting the counter to work for particles entering through all parts of the ring. Best results were obtained with a counter of 1·3 to 1·5 cm. inside diameter with the end facing the ring completely open, and about 1 mm. away from the mica window. The point must be exactly central and about 4 cm.

back from the mica window The counter was worked between 900 and 1,000 volts, and about half an atmosphere pressure depending on the sensitivity of the point Steel points were used as they are easy to grind

It was found advisable to measure the fraction of the ring cut off by the shutter in positions (4) and (5) by counting with the same source used to check the action of the counter over the whole annular ring rather than by measuring the amount cut off by means of a travelling microscope or attempting to make it exactly half

The scattering material used was gold because it can be obtained in fairly uniform thin sheets The value of nt could be calculated either from weighing a large piece of gold leaf and using a sample of it for the experiment or by measuring the stopping power of several layers of the gold leaf The first gives much too low a value as in the weighing of a large piece many holes cannot be accounted for and in choosing a piece for the experiment a very uniform piece is naturally taken The results show that the second method worked much better though it cannot be considered as accurate because the actual piece used in measuring the stopping power cannot be used in the experiment Mr F Oldham kindly measured for me the stopping power of some samples of gold leaf by an accurate ionization method It was considered not advisable in these experiments to concentrate on an absolute measurement of the amount of scattering but rather to compare the number scattered at different angles for previous experiments have shown that under certain conditions the amount of scattering agrees very closely with that predicted by the nuclear theory

A source of polonium was used for the main part of the experiment as it gives only alpha rays and has a suitably long period It was found that sources which give beta and gamma rays could not be used with the electrical counter, because the gamma rays caused a much greater effect than the relatively small number of alpha rays which pass through the annular ring As the aperture A was necessarily small (0 0828 cm diam), the area of the surface on which the polonium could be effectively deposited was small but it could be increased to between 2 and 3 sq mm by making the source holder in the shape of a conical point Even with this area it was found impossible to get a sufficiently large source to make counting easy The polonium was deposited on nickel by the method described by Mlle Irene Curie,* but it seemed that as soon as any appreciable quantity was deposited the action ceased, probably on account of the intense ionisation due to the material already deposited After repeated attempts Dr Chadwick who kindly prepared the sources for the experiment succeeded in depositing about 0 2 mg activity of polonium on the point With this quantity the alpha particles came through the annular ring at the rate of about three per minute when the apparatus was set so that they were deflected through angles of about 6 degrees. With this source the mica window M was omitted as the velocity of alpha particles from polonium (range 3 925 cm) was suitable for the experiment

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* Thesis, Paris.

The number of alpha particles from the source was measured by another counter placed on the end of a long glass tube The source was placed symmetrically in the tube about 60 cm from a small opening into the counter and ebonite stops were put in the tube about every 15 cm to prevent particles scattered from the walls of the tube from getting into the counter The whole tube was then evacuated The strength of the source was measured in this apparatus before and after the experiment

The results were checked using a source of thorium active deposit a larger quantity of which could be deposited on a small platinum surface For this source the mica window M was used to cut out the short range particles and to cut down the velocity of the long range particles to that corresponding to a range of about 4 cm In this case the scintillation method of counting the alpha particles had to be used because as mentioned before the gamma rays caused many more deflections with the electrical counter than the small number of alpha particles passing through the ring The size of this source was measured by letting it decay for a day and then counting the number of particles coming through the hole in the centre of the annular ring the scattering foil having first been removed As only relative results were used in this part of the experiment it was not necessary to know the activity of the source accurately The whole apparatus was placed between the poles of a large electro magnet in order to deflect the beta rays away from the screen

Results and Conclusions

Two separate runs were taken with the polonium source For the first, the results of which are plotted in fig 3 two layers of gold leaf were used as the scattering material The full curve represents the relation

$$y = \frac{35\ 07}{\phi^2}$$

The broken curve and the points marked represent the experimental results. The curve fits the observations fairly well at angles greater than about 2 5 degrees.

The deviation at smaller angles is probably due to multiple or plural scattering. At larger angles single scattering alone is effective. As the angle of scattering

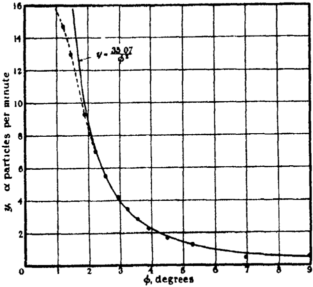

FIG. 3

decreases the effects of plural scattering become apparent, and the amount of scattering should first increase slightly above that of pure single scattering and then decrease below it at still smaller angles. A tabulation of the results shows this to be the case (see Table I). The first column is the average angle ϕ at which the scattering was observed. The second is the number of alpha-particles scattered at this angle per 1,000 particles incident on the scattering foil. The third column is the product $y\phi^2$. In the fourth column the number of alpha-particles counted at each point is tabulated to show the accuracy of the experiment. The first four points show multiple scattering so are not tabulated in column 3.

From equation (6) the product $y\phi^2$ should be a constant. Column 3 shows that it approaches a maximum and then decreases. This would be the expected result of plural scattering. The last four points are rather erratic, which is to be expected due to the small number of particles counted. Any great accuracy at these points was out of the question because the rate of counting was from 1 to 3 alpha-particles per minute, and the natural count of the counter

Table I

Average Angle Degrees	y	$y\phi^2$	Number Counted
1 21	14 7	—	305
1 45	13 05	—	644
1 89	9 25	—	842
2 21	6 96		211
2 54	5 50	35 5	1 124
2 94	4 17	36 1	740
3 24	3 46	36 2	753
3 55	2 81	35 4	627
3 80	2 24	33 9	797
4 49	1 63	32 7	433
5 29	1 24	34 6	60
6 97	0 40	19 5	30
8 97	0 48	38 6	30

was usually from 2 to 4 particles per minute The constant 35 07 used in plotting the curve drawn in full in fig 3 is the weighted mean of $y\phi$ in Table II from the point $\phi = 2\ 94$ to the point $\phi = 4\ 49$ degrees inclusive The theoretical value of this constant calculated from measurements of the stopping power of the gold leaf is 32 2 The observed value would probably approach this closely at about 6 degrees

Fig 4 and Table II represent the results for one layer of gold leaf as the scattering material The weighted mean value of K in this case is 15 17 using all points except the first It is rather off the curve as would be expected

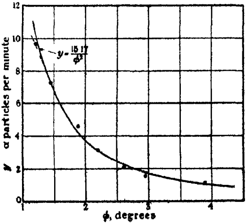

Fig 4

Table II

Average Angle Degrees	y	$y\varphi^2$	Number Counted
1 21	0 66	14 1	1 547
1 45	7 24	15 2	1 253
1 80	4 01	16 4	837
2 21	3 15	15 5	750
2 54	[illegible]	13 6	581
2 94	1 64	13 4	520
3 89	1 11	16 8	311

due to plural scattering The calculated value of the same content is 16 1 This would indicate that the effect in this case was all due to single scattering but as pointed out before the foil used for calculating the constant could not be the one used in the experiment so very close agreement should not be expected

The K Shell of Electrons

It might be expected that the alpha particles which passed at a distance from the nucleus nearly equal to the radius of the K shell of electrons would be affected more than the others If a considerable number of these ionize the K shell in some way or other these particles would probably be further deflected This would leave a depression with a minimum in the scattering curve at an angle where the nearest distance of approach of the alpha particle to the nucleus is equal to the radius of the K shell A suggestion of such a minimum may be seen in the curve in fig 4 The points at 2 54 and 2 94 degrees are much lower than the theoretical curve and seem to indicate a minimum at about 2 7 degrees The nearest distance of approach of the alpha particle to the nucleus for this angle on an inverse square law of force is 0 86 $\times 10^{-10}$ cm. This is calculated on the assumption that the nuclear charge is effectively $79e$, or that there is no shielding effect due to the inner electrons Assuming a shielding of $2e$ for the K shell this same distance becomes 0 84 $\times 10^{-10}$ cm This is about 22 per cent larger than 0 69 $\times 10^{-10}$, which is the value calculated from Bohr s atomic model As it does not appear at all on the curve in fig 3, though the effect would be considerably masked by multiple scattering it is quite likely that it is merely a probability variation Taking this view the results would show that the probability of an alpha particle ionizing the K shell is quite small The mechanism of such an ionization is difficult to imagine because the velocity of the electron according to Bohr's theory is more than 11 times that of the alpha particle Treating a nearly head-on collision between the two as a two-body problem, the force being attractive, it may be shown by conservation of energy and momentum laws that the direction of motion of the electron would be reversed and its velocity reduced, hence, because the forces are attractive, the electron gives energy to the alpha-particle instead of receiving energy from it However, the alpha-particle has enough energy to ionize the K shell and as it is not unlikely that the mechanism of such a collision may be affected by the nucleus or by some kind of quantum conditions such an ionization is not impossible

When the nearest distance of approach of the alpha-particle to the nucleus is equal to the radius of the K shell calculated from data on K absorption limits and Bohr's model of the atom the deflection based on the inverse square law should be 3 87 degrees At much larger angles the alpha-particles penetrate well into the K shell and should be scattered according to Rutherford's relation At smaller angles, that is a greater value of p, the shielding effect of the K shell, if there is any, should cause a smaller deflection than if it were not there If there is a shielding effect of $-2e$ the number of alpha-particles deflected through angles less than 3·78 degrees would be $(77/79)^2$ times what would be otherwise expected That would mean an ascending value of $y\phi^2$ as the angle was increased instead of descending as the tabulations show. Unfortunately, owing to the small activity of the polonium source, it was impossible to obtain a proper test for this effect A further attempt, however, was made with a thorium B and C source

In order to increase the accuracy, all the counting was concentrated on two points, 2 21 degrees and 4·58 degrees, so that a large number of particles could be counted for each point The ratio of the number of particles counted at these points should be, if there were no shielding, equal to the inverse ratio of the squares of the angles, namely 4·29 Using one layer of gold leaf as the scattering material the experimental ratio was 4·43 with a probable error of about 8 per cent. With two layers of gold leaf the ratio came to 5·58 with a probable error of about 10 per cent. Enough particles were counted to give much greater accuracy than this, but a great deal of difficulty was experienced due to contamination of the zinc-sulphide screen during the course of the experiment. The natural count of the screen had to be taken several times throughout each series of counts, the results plotted and the correction taken from points on the curve corresponding to the time of the counting with the annular ring open. Usually at the beginning of the run the contamination was of the same order as the number of particles passing through the ring at the larger angles, 5 to 7 alpha-particles per minute for most runs. The larger angles had to be treated first in order to get a sufficient number of particles before much of the source was lost by decay

Inverse Square Law

Other experiments, previously mentioned, on the scattering of alpha-particles by gold have shown that the field surrounding the nucleus obeys the inverse square law of forces fairly closely at distances from $3 \cdot 2 \times 10^{-12}$ cm. to $5 \cdot 1 \times 10^{-11}$ cm from the nucleus The main part of this range was covered by Geiger and Marsden in their experiment to test the nuclear theory Their experimental results for the relative scattering by gold at different angles agreed to within about 20 per cent of those predicted by theory for particles whose nearest distance of approach to the nucleus was from $4 \cdot 6 \times 10^{-12}$ cm. to $5 \cdot 1 \times 10^{-11}$ cm Rutherford and Chadwick tested the region from $3 \cdot 2 \times 10^{-12}$ cm to $6 \cdot 5 \times 10^{-12}$ cm much more accurately Their results are within 10 per cent of those predicted by theory They measured not only relative scattering but also absolute scattering, and from the experimental results deduced the nuclear charge for gold It agreed to within 2 per cent of the atomic number times the elementary charge This gave a check against Chadwick's results with platinum as the scattering material He deduced the nuclear charge from his experimental results to within about 1 per cent. of the atomic number times the elementary charge and also showed that the inverse square law was obeyed for particles whose nearest distance of approach to the nucleus was from 7×10^{-12} cm to 14×10^{-12} cm The results of the present experiment indicate that the nuclear field obeys the inverse square law fairly closely for distances from $0 \cdot 4 \times 10^{-10}$ cm to $1 \cdot 7 \times 10^{-10}$ cm or to about $2\frac{1}{2}$ times the radius of the K shell. For most of the points more than 600 alpha-particles were counted, so the probable error should be about 4 per cent, but deviations due to multiple scattering and possibly due to the K shell of electrons, as suggested previously, make it difficult to say to what accuracy the inverse square law holds. It would certainly be considerably better than 10 per cent. A calculation based on measurements of the stopping power of samples of the gold foil give a value for the constant K in equation (6), within 10 per cent. of the experimental value As K, on the nuclear theory, is proportional to N^2, the experimental determination of the atomic number N is within about 5 per cent. of the known value. Hence, we may conclude that for distances from the nucleus from $3 \cdot 2 \times 10^{-12}$ cm to $1 \cdot 7 \times 10^{-10}$ cm the inverse square law holds and the effective nuclear charge at these distances is within 5 per cent. or less of the atomic number times the elementary charge.

Criterion for Single Scattering

As mentioned previously Wentzel's criterion for single scattering says that, as long as ϕ is considerably greater than 4ω one can be sure of single scattering ω being the angle of single scattering corresponding to $p = \sqrt{\frac{2}{\pi nt}}$ but he gives no information as to how much greater or how many times 4ω the angle ϕ should be For one thickness of the scattering foil used the value of nt as measured by the stopping power is $0\ 73 \times 10^{18}$ The corresponding value of 4ω is 1 degree 4 minutes For two thicknesses of the scattering foil 4ω is 3 degrees Examining the curves in figs 3 and 4 and Tables I and II it is seen that the results agree with the theoretical value of $y\phi^2$ very closely at somewhere about 6 or 7 degrees in the case of two foils and about 2 25 degrees in the case of one foil This means that it would be safe to say that so long as ϕ is not less than 10ω one can be sure that the effect is practically all due to single scattering

Summary

The single scattering of alpha particles through angles from 1 2 degrees to over 8 degrees has been measured The scattering material used was gold

The scattering curves indicate that the nuclear field obeys the inverse square law fairly closely for distances from $0\ 4 \times 10^{10}$ cm to $1\ 7 \times 10^{10}$ cm from the nucleus Other experimenters have shown that the inverse square law of force holds up to $3\ 2 \times 10^{12}$ cm from the nucleus The results are not accurate enough to detect any shielding effect due to the K shell of electrons

The curves indicate that the K shell is not ionized to any appreciable extent

Wentzel's criterion for single scattering has been extended The effect is practically all due to single scattering when the scattering angle ϕ is not less than 10ω where ω is the angle of single scattering corresponding to $p = \sqrt{\frac{2}{\pi nt}}$

In conclusion, I wish to express my thanks to Sir Ernest Rutherford for continued interest and to Dr J Chadwick for suggestions and preparation of sources

The Structure of Beryl, $Be_3Al_2Si_6O_{18}$

By W LAWRENCE BRAGG, F R S , Langworthy Professor of Physics,
Manchester University, and J WEST, John Harling Fellow, Manchester
University

(Received May 21, 1926)

1 The structure of beryl described in this paper, has some interesting features In the first place, the ratio of silicon to oxygen atoms in the molecule is that of a metasilicate As far as we know, no other example of a metasilicate has as yet been completely analysed (Wyckoff* has made some measurements on diopside $MgCa(SiO_3)_2$, but has only succeeded in determining its space group) Although the ratio of silicon to oxygen is as one to three we find no SiO_3 groups in beryl We find instead an arrangement of oxygen atoms around a silicon atom of exactly the same conformation as the groups $(SiO_4)^{--}$ in typical orthosilicates such as olivine† and garnet ‡ In this metasilicate the ratio of one silicon to three oxygen atoms is effected by a sharing of two oxygen atoms of each tetrahedral SiO_4 group with neighbouring groups Thus the structure forms an intermediate stage between the orthosilicates and the structures of quartz§ and christobalite|| where every oxygen atom is shared by silicon atoms This interesting feature may throw some light on the structure of other metasilicates In the second place, we have analysed the structure by making careful quantitative measurements of the absolute intensity of X ray reflexion, and interpreting these measurements by the formulæ which have proved to hold for simpler cases The structure is one of moderate complexity, depending on seven parameters We hope to show that all these parameters can be directly and accurately fixed The analysis is greatly simplified when quantitative data are available, and there appears to be no reason why structures with many more parameters should not be attacked in the same direct manner

2 Beryl belongs to the holosymmetric class of the hexagonal system Groth (' Chemische Krystallographie ') quotes the axial ratio—

$$a \quad c = 1 \quad 0\ 4989,$$

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* Wyckoff, ' Am Journ Sci ,' vol 9, p 379 (1925).

† W L Bragg and Brown, Zeitschr für Kristallogr ' (1926)

‡ Menzer, ' Zeitschr für Kristallogr ,' vol. 63, p. 157 (1926)

§ W H. Bragg and Gibbs, ' Roy Soc Proc ,' A, vol 109, p 405 (1925).

|| Wyckoff, ' Am. Jour Sci.,' vol 9, p. 448 (1925)

and gives the density as being between 2·6 and 2·7. We have found the following values for the axes, measured by the X-ray spectrometer—

$$c = 9 \cdot 17 \pm 0 \cdot 01 \text{ Å}$$

$$a = 9 \cdot 21 \pm 0 \cdot 01 \text{ Å}$$

These lead to an axial ratio—

$$a : c = 1 : 0 \cdot 9956,$$

the *c* axis being twice as long as is ordinarily assumed. Since these are the true axes of the space group, they will be used below. The plane usually termed (1011), for instance, will here be given its true indices $(10\bar{1}2)$.

Calculation shows that the unit cell of the hexagonal space lattice contains two molecules of $Be_3Al_2Si_6O_{18}$. The X-ray measurements lead to a value 2·661 for the density.

Four space-groups may correspond to a structure of the dihexagonal bipyramidal class. They are distinguished as follows —

D^1_{6h} No abnormal spacings
D^2_{6h} $(m\ o\ \bar{m}\ l)$ and $(m\ m\ \overline{2m}\ l)$ halved if l is odd
D^3_{6h} $(m\ o\ \bar{m}\ l)$ halved if l is odd
D^4_{6h} $(m\ m\ \overline{2m}\ l)$ halved if l is odd.

A survey of the observed reflexions shows that the beryl structure is based on the space group D^2_{6h}.* The following reflexions were investigated —

Type $\{000l\}$	Present. Even orders up to 000 20
	Absent. Odd orders up to 000 19
Type $\{m\ o\ \bar{m}\ o\}$	All orders up to eighth present
Type $\{m\ m\ \overline{2m}\ o\}$	All orders up to eighth present, with exception of seventh order
Type $\{m\ o\ \bar{m}\ l\}$	Present $(10\bar{1}2)$. $(40\bar{4}8)$, $(10\bar{1}4)$ . . $(30\bar{3}12)$, $(10\bar{1}6)$, $(20\bar{2}.12)$, $(10\bar{1}8)$, $(20\bar{2}2)$, $(40\bar{4}4)$, $(60\bar{6}6)$
	Absent $(10\bar{1}1)$, $(30\bar{3}3)$, $(50\bar{5}5)$, $(70\bar{7}7)$, $(10\bar{1}3)$, $(10\bar{1}5)$

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* *Cp.* Niggli, 'Geometrische Krystallographie des Discontinuums,' p. 350 (1919). We have referred below to the adaption of space-group theory to X-ray analysis by Astbury and Yardley, rather than to the pioneer work of Niggli in this field, or to that of Wyckoff, because the later treatment gives the results in so convenient and compact a form.

Type $\{m\,m\,\overline{2m}\,l\}$ Present $(11\bar{2}2)$ . . $(66\overline{12}6)$, $(22\bar{4}2)$, $(11\bar{2}4)$, $(22\bar{4}8)$
$(11\bar{2}6)$, $(22\bar{4}12)$, $(11\bar{2}8)$
Absent $(11\bar{2}1)$, $(11\bar{2}3)$, $(11\bar{2}5)$, $(11\bar{2}7)$, $(22\bar{4}1)$, $(33\bar{6}1)$,
$(33\bar{6}3)$, $(55\overline{10}5)$, $(66\overline{12}3)$, $(77\overline{14}7)$, $(99\overline{18}3)$.

General type Present $(12\bar{3}1)$ .. $(48\overline{12}4)$, $(31\bar{4}1)$, $(3\bar{1}\bar{2}1)$. $(12\bar{4}\bar{8}4)$,
$(5\bar{2}\bar{3}3)$, $(4\bar{1}\bar{3}1)$, $(12\bar{3}\bar{9}3)$

It is only in the planes of the general type that the true length of the "*c*" axis is apparent Since planes $(m\,o\,\bar{m}\,l)$ and $(m\,m\,\overline{2m}\,l)$ are halved if l is odd, the space group must be D$^2_{6h}$

3 The symmetry elements of D$^2_{6h}$ are shown in fig 1, which is a copy of the corresponding figure due to Astbury and Yardley * The conventions adopted to indicate the symmetry are described in their paper A group of formula $Be_6Al_4Si_{12}O_{36}$, lies in each unit cell

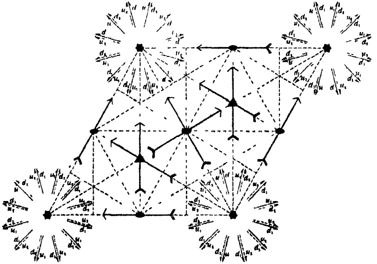

FIG. 1.—Symmetry Elements of Beryl (*c* axis parallel to plane of paper)

It will be seen from the figure that there are sixfold, threefold and twofold axes parallel to the *c* axis Reflexion planes of symmetry perpendicular to the *c* axis exist at heights $c/4$, $3c/4$ from the base of the unit cell The planes at heights 0, $c/2$, c are occupied by a network of twofold axes, those at a height c being shown in the figure as thick arrows. There are a number of glide planes shown as dotted lines, parallel to the hexagonal axis.

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* Astbury and Yardley, 'Phil. Trans. Roy. Soc.,' A, vol. 224, p. 221 (1924).

An atom in the general position is multiplied by the operations of symmetry into 24 within the unit cell. Since the group within the cell is $Be_6Al_4Si_{12}O_{36}$, the only atoms in the general position can be a group of 24 oxygen atoms. As we shall see, all other atoms lie in positions at heights 0, $c/4$, $c/2$, $3c/4$ in the unit cell. This indicates a very simple structure for the planes (000l), and we will analyse these in the first place.

The intensities of reflexion were in all cases compared with the reflexion NaCl (400) as standard, RhK$_\alpha$ rays being used. The absolute values for the integrated reflexion ρ for the planes (000l) are given below.

Table I.—$\rho \times 10^6$, (000l) planes.

(0002)	160	(000·12)	19
(0004)	104	(000·14)	10
(0006)	111	(000·16)	3·5
(0008)	92	(000·18)	nil
(000·10)	4·0	(000·20)	3·0

The intensities were measured by rotating the crystal with uniform angular velocity ω, and measuring the total ionization E produced as it passed through the reflecting angle. We assumed the value $E\omega/I = 100 \times 10^{-6}$ for the integrated reflexion NaCl (400), in order to determine the power I of the incident X-ray beam.

The high symmetry limits the positions in which the atoms of the group $Be_6Al_4Si_{12}O_{36}$ may be placed. The four aluminium atoms must either be placed in a row on the hexagonal axes (a very improbable arrangement, since they would then approach each other so closely) or they must be on the trigonal axes. In the latter case they either lie at heights 0, $c/2$, or at heights $c/4$, $3c/4$ from the base of the unit cell. If we assume that the trigonal axes are occupied by the aluminium atoms, the six beryllium atoms can only be equivalent and lie on the twofold axes parallel to c. Like the aluminium atoms, they lie either at heights 0, $c/2$, or at heights $c/4$, $3c/4$. In the case of the twelve silicon atoms we may again assume it highly improbable that they should be arranged in rows on the vertical axes. Alternatively, they may lie in two rings of six atoms around the hexagonal axes, being in this case all equivalent to each other. These rings lie at heights 0, $c/2$, or $c/4$, $3c/4$ in the unit cell. In the former case each silicon lies on a twofold axis perpendicular to the c axis, in the latter case on a reflexion plane parallel to (0001) Twelve of the oxygen atoms are governed by exactly the same conditions as the twelve silicon atoms The remaining twenty-four atoms lie in the general position, and hence have a parameter parallel to the c axis

From the foregoing it will perhaps be clear that in explaining the strength of the $(000l)$ spectra we have a limited number of alternatives to test, and that in each case there is only a single parameter (governing the c displacement of twenty-four oxygen atoms) which can be adjusted to give a correspondence between calculated and observed intensities It is therefore a simple matter to choose between these alternatives The only arrangement which corresponds with the spectra is shown in fig 2

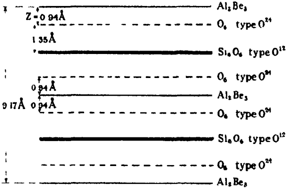

FIG 2 —Arrangement of Atoms in planes parallel to $(000l)$, Beryl.

The intensities of reflexion from planes $(000l)$ are decidedly stronger when l is a multiple of four than when l is a multiple of two, especially in the higher orders This proves that the planes containing silicon must alternate with those containing aluminium, since the effect of the oxygen atom rapidly becomes very small as the angle of reflexion is increased The effect of the beryllium atoms is small, but it is sufficient to make it possible to say that they lie in the planes containing aluminium atoms when the final quantitative examination of intensities is carried out as described in the next paragraph. One-third of the oxygen atoms lie in the same planes as the silicon atoms The remainder lie in the general position. Their displacement parallel to the c axis is fixed by the distance z indicated in fig 2. The general features of the intensities show immediately that z has a value of about 0·94 Å. This position is required, for instance to explain the strength of (0006) and the weakness of (000 10) The type of analysis which leads to this result is so well known that it is perhaps unnecessary to go into it further here

The question as to whether the groups Si_6O_6 or Al_2Be_3 lie on the reflexion planes perpendicular to the c axis may be left open for the present since it does not affect the discussion of intensities in the next paragraph Other considerations show that the groups Si_6O_6 lie on these planes

4 The formula for the absolute intensity ρ of integrated reflexion by the face of an imperfect crystal is as follows —* † ‡

$$\rho = \frac{E\omega}{I} = \frac{1}{2\mu} n^2 \lambda^3 F^2 \frac{e^4}{m^2 c^4} \frac{1}{\sin 2\theta} \frac{1 + \cos^2 2\theta}{2} e^{B \sin \theta} \qquad (1)$$

In this formula the symbols have the following meaning —

μ — linear absorption coefficient of crystal

n — number of unit cells in one cubic centimetre

λ — wave length of X rays

e = electronic charge

m = electronic mass

c = velocity of light

θ = glancing angle of incidence

$e^{B \sin^2 \theta}$ is the temperature factor first introduced by Debye

The symbol F stands for the ratio of the amplitude of the wave scattered by all atoms in the unit cell in the direction under consideration as compared with the wave scattered by a single electron in similar circumstances The value of F varies with the direction of the incident and scattered X ray beam The contribution of each atom to the scattered wave will depend on the arrangement of the electrons in the atom and the combination of these contributions into a single scattered wave will depend on the relative positions of the atoms in the unit cell

In the present analysis we will use the observed intensities of X-ray reflexion to determine F for a number of crystal planes From these values of F the atomic positions will be directly deduced

F can be calculated from formula (1) by using the observed values of ρ and substituting known values for the other factors which appear The only quantity which needs especial consideration is the absorption coefficient μ When a crystal has more than a certain degree of perfection, the effective absorption coefficient is increased by "primary" and "secondary" extinction, very fully discussed by Darwin in his 1922 paper cited above In the case of certain (000*l*) reflexions from beryl, the structure is sufficiently well known to a first approximation for it to be possible to calculate values of F which cannot be far from the truth Using these in formula (1), a comparison with the observed values of ρ show that extinction is appreciable, being of the same order as the normal absorption coefficient in the case of the strongest reflexions

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* Darwin, Phil Mag vol 27 pp 315 and 675 (1914) vol. 43, p. 800 (1922)

† Compton, A. H Phys Rev vol. 9 p 29 (1917)

‡ Bragg James and Bosanquet, Phil Mag vol. 41 p 309 (1921) vol. 42, p 1 (1921), vol 44 (Sept 1922) James and Randall, vol. 1 p. 1020 (1926)

Our procedure has been as follows We have assumed that we can represent the effective absorption coefficient μ by the formula

$$\mu = \mu_0 + \alpha\rho \tag{2}$$

μ_0 is the normal absorption coefficient, ρ the intensity of reflexion and α a constant characteristic of the particular specimen of crystal being examined and an index of its perfection In a highly imperfect crystal α is zero This formula is empirical, but there is some justification (experimental and theoretical[*][†]) for using it, especially when extinction is not very large as in the present case With this assumption, we can write formula (1) as follows (neglecting the final temperature factor, which is probably small in so hard a crystal) —

$$\rho = \frac{1}{\mu_0 + \alpha\rho} \mathrm{A} \ \mathrm{F}^2 \ \Theta \tag{3}$$

Here

$$\mathrm{A} = \tfrac{1}{4}\frac{n^2\lambda^3 e^4}{m^2 c^4} = 1\ 01 \times 10^{-8} \text{ for beryl}$$

$$\Theta = \frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

The value of μ_0 for beryl, based on Windgärdh's[‡] tables, is 5 64

We now consider the planes (000*l*) which have a very simple structure The scattering curves for beryllium, aluminium, silicon and oxygen are taken from the tables prepared by Hartree, these being slightly modified by the results of quantitative measurements made on certain simple crystals The values of the scattering power of the atoms as compared with that of a single electron are given for a series of angles at the end of the paragraph In comparing calculated and observed values of ρ in order to get the best agreement, there are two variables which can be adjusted; these are the distance z, determining the position of the 24 oxygen atoms (paragraph 3), and the coefficient α, which determines extinction It has already been seen that z has a value of about 0 94 Å This value will be assumed for a first approximation, and formula (3) checked, using a series of values of α in order to discover the one which gives the best agreement It is perhaps simplest to show this agreement by calculating A from the observed intensities, using formula (3) and comparing it with what is known to be the right value, $1\ 01 \times 10^{-8}$

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[*] Darwin, *loc cit*

[†] Bragg James and Bosanquet James and Randall, *loc cit*

[‡] Windgårdh, Zeitschr f Phys, vol. 8, p 363 (1922)

Table II

Indices	$\rho \times 10^4$	$F^2\Theta \times 10^{-4}$	$A = \left(\frac{\rho(5\ 64 + \alpha\rho)}{F^2\Theta}\right) \times 10^8$			
			$\alpha = 0$	$\alpha = 6 \times 10^4$	$\alpha = 7 \times 10^4$	$\alpha = 8 \times 10^4$
(0002)	1 60	27 5	0 33	0 88	0 98	1 07
(0004)	1 04	13 4	0 43	0 92	1 00	1 09
(0006)	1 11	14 1	0 44	0 97	1 04	1 14
(0008)	0 92	11 6	0 45	0 88	0 98	1 03

It is clear that the assumption of no extinction leads to obviously incorrect values The value 7×10^4 for the coefficient α gives both the best correspondence between values of A calculated from different spectra, and the best agreement with the true value $1\ 01 \times 10^{-8}$ This value for α will therefore be chosen A knowledge of α makes it possible to correct for extinction, and to substitute for the observed reflexion ρ the idea reflexion ρ' which would be observed with an ideally imperfect crystal All our observations have been corrected in this way, and used to determine the values of F for each reflexion.

We can now make a final adjustment by seeing whether a better estimate of the distance z can be obtained when extinction is allowed for. The value of 7×10^4 for α is assumed, and A calculated for a series of values of z

Table III

Indices.	Values of A for distances z of oxygen atoms from Al_2Be_3 planes in Å							
	1 02	1 00	0 98	0 96	0 94	0·92	0 90	0 88
(0002)	0 73	0 78	0 83	0 90	0 98	1·05	1 13	1 21
(0004)	1 22	1 19	1 13	1 06	1 00	0 93	0 88	0·83
(0006)	1 33	1 28	1 18	1 12	1 04	0 99	0 96	0 92
(0008)	0 76	0 81	0 85	0 90	0·98	1 02	1 09	1 17

The value 0 94 already assumed is seen to be the best and z appears to lie definitely between 0 92 Å and 0 96 Å The oxygen atom is therefore at a distance of 1 35 Å from the planes Si_6O_6 as shown in fig 2

The following table gives the values of F for the atoms Be Al Si O which have been used in the calculations —

Table IV Values of F

Sin θ	0 0	0 1	0 2	0 3	0 4	0 5	0 6
Beryllium	2	1 95	1 65	1 60	1 35	1 05	0 75
Aluminium	10	9 55	8 30	6 65	4 90	3 45	2 25
Silicon	13	7	9 4	7 4	5 6	4 2	2 8
Oxygen	9	6 9	3 6	1 6	0 5	0 2	0 1

It is difficult to decide what initial values of F to adopt We have chosen the values 13 and 9 for silicon and oxygen in an attempt to allow for the distortion of the oxygen atoms grouped around the silicon atom If the figures 10 and 10 had been chosen a test shows that the position assigned to the atom would be almost exactly the same The former figures however do undoubtedly give a more consistent agreement with observed intensities The form of the F curves beyond sin θ = 0 2 is taken from Hartree s tables and the curves continued on to the maxima 13 and 9 for silicon and oxygen respectively

5 The symmetry elements of the unit cell are shown in fig 1 The atoms have to be arranged in accordance with these symmetry elements and in a way which explains the observed intensities of spectra Certain general considerations lead at once to an approximate solution of the structure

The distance between neighbouring oxygen atoms may be expected to be about 2 7 Å W L Bragg and G Brown* have pointed out that this is the case in BeO Al_2O_3 $BeAl_2O_4$ Mg_2AlO_4 and Mg_2SiO_4 In the structure of garnet $Ca_3Al_2Si_3O_{12}$, recently analysed by Menzer † the distance between neighbouring oxygen atoms varies from 2 65 to 2 85 Å James has shown that this interatomic distance exists in $BaSO_4$ ‡ and Wasastjerna in $CaSO_4$ § Fig 2 shows that the twenty four oxygen atoms in the general positions are arranged on sheets parallel to (0001) which are at a distance of 0 94 Å on either side of the planes marked Al_2Be_3, and at a distance of 1 35 Å on either side of the planes marked Si_6O_6 If the distance between oxygen atoms is to be about 2 7 Å in

* W L Bragg and Brown Roy Soc Proc A vol 110 p 34 (1926)

† *Loc cit* paragraph 1

‡ James and Wood Roy Soc Proc A vol 109 p 598 (1925)

§ Wasastjerna, Soc Scient Fenn Comm Phys Math vol 2 p 26 (1926) beryl, it is at once clear that these latter planes are the reflexion planes of the structure each oxygen atom being at a distance of 2 7 Å from its mirror image If this were not the case and the planes marked Al_2Be_2 were the reflexion planes,

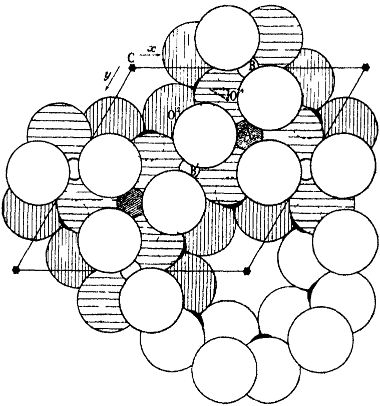
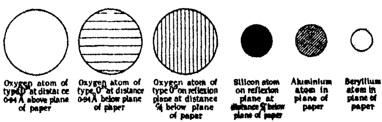


FIG. 3.—Diagram of Beryl Structure viewed parallel to c axis showing positions of half the atoms in the unit cell


Oxygen atom of type O^1 at distance 0·94 Å above plane of paper
Oxygen atom of type O^2 at distance 0·94 Å below plane of paper
Oxygen atom of type O^3 on reflexion plane at distance $c/4$ below plane of paper
Silicon atom on reflexion plane at distance $c/4$ below plane of paper
Aluminium atom in plane of paper
Beryllium atom in plane of paper

KEY TO FIG 3

the distance between oxygen atoms would be 1 9 Å, which is too small to be probable

In fig 3, the lines indicate the upper sides of the unit cell The aluminium and beryllium atoms lie in this upper plane, and the reflexion plane is at a distance $c/4$ (2 29 Å) below One of the twenty-four oxygen atoms which are in the general position will lie within the confines of the triangle ABC, and at a distance 0 94 Å beneath the plane of the diagram (the alternative position in the triangle AB′C is not distinct, since it is only necessary to translate the origin of co-ordinates a distance $c/2$ to arrive at it) This atom is lightly shaded, and is marked O^{24} in the figure Three twofold axes at right angles to each other intersect in the Be atom at B, and these axes convert the oxygen atom at O^{24} into a tetrahedral group around B

Assuming that no oxygen atom approaches much closer than 2 7 Å to any other oxygen atom, the possible positions for the atom O^{24} are very limited It must not be closer than about 1 35 Å to any twofold axis, or to the reflexion plane (we have already shown that it is actually at a distance of 1 35 Å from the reflexion plane) It must not lie closer than $\frac{2}{\sqrt{3}} \times 1\ 35$ Å to a trigonal axis, or $2 \times 1\ 35$ Å to a hexagonal axis, or it will be too close to the other atoms around these axes If we assume as an extreme case that the atoms may approach within 2 5 Å of each other, trial shows that the atom is confined to the small triangular area around O^{24} outlined in the figure If one atom is placed anywhere in this region, the others into which it is turned by the symmetry elements will have the positions indicated in the figure by the unshaded and lightly-shaded circles The unshaded circles are at a height 0 94 Å above the plane, the lightly-shaded circles at a depth 0 94 Å below it Each beryllium atom lies at the centre of four oxygen atoms arranged tetrahedrally, every aluminium atom at the centre of six oxygen atoms arranged at the corners of an octahedron

The aluminium, beryllium, and twenty-four of the oxygen atoms are thus accounted for It remains to place the twelve silicon atoms and twelve oxygen atoms of the second sort on the reflexion planes at a depth $c/4 = 2\ 29$ Å below the plane of the diagram. The oxygen atoms will lie in groups of six around the hexagonal axes, and there is just room for such a group, indicated by the heavily-shaded circles The typical atom of this group is marked O^{12} in the figure. Each pair of heavily-shaded atoms lying in the reflexion planes forms a tetrahedral group with a pair of lightly-shaded atoms which are images of each other in the plane This suggests that the silicon atoms may be at the centre of these tetrahedra, and this supposition will be tested. The silicon atoms would be invisible in the structure as represented here, but for the sake of clearness their positions are indicated by the portions of black circles, continued as dotted lines The diagram in fig 3 shows the positions of those atoms which are grouped on either side of the reflexion plane at a depth of $c/4$ A similar group, obtained from the first by rotation about an axis at a depth of $c/2$, is placed on either side of the reflexion plane at a depth $3c/4$, but is not shown in the figure

The positions finally assigned to the atoms depend in no way on assumptions as to interatomic distance This preliminary investigation merely indicates probable values for the parameters and so shortens the analysis

6 *Determination of Parameters*—The structure has seven parameters, of which one has been already determined The parameters fix the positions of the silicon atoms (two parameters), the twenty-four oxygen atoms of the first type (three parameters), and the twelve oxygen atoms of the second type (two parameters)

Since the only parameter parallel to the c axis is known, the rest can be got by considering the projection of the structure on (000l) and examining the planes around the c zone The silicon and oxygen atoms lie in rings of six around the hexagonal axes We have found it convenient to consider the ring as a diffracting unit when dealing with planes around the c zone The resultant scattered wave of six atoms in a ring will have the same phase as that of a wave scattered from a point at the centre The ratios of the contribution of the six atoms to that of a single atom at the centre depends on—

(*a*) The ratio nr/d where "r" is the distance from the centre to each atom "d" the spacing of the reflecting planes, "n" the order of the spectrum

(*b*) The angle β made by the line, joining the centre of the ring to one of the atoms, with the reflecting planes The angle β need only be considered to vary between 0° and 30° owing to the repeat of the atoms around the hexagonal ring.

We have plotted curves showing the value of the ratio for values of nr/d up to 7 0, and for several values of β Some of the curves are shown in fig. 4 The ratio is given by the expression

$$S = 2\left\{\cos\left(\frac{2\pi nr}{d}\sin\beta\right) + 2\cos\left(\frac{\sqrt{3}\pi nr}{d}\cos\beta\right)\cos\left(\frac{\pi nr}{d}\sin\beta\right)\right\}. \qquad (4)$$

These curves can be used for any case where the projection of a structure on a plane has hexagonal symmetry, such as the planes around certain zones of the

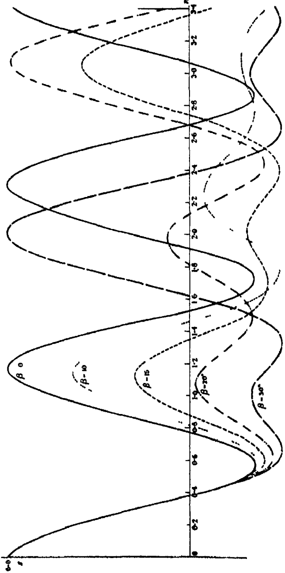

β 0
β = 10
β = 15
β = 20°
β = 30°
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
2·8
3·0
3·2
3·4
6·0
s

FIG 4

cubic or trigonal classes when these have a centre of symmetry as well as for hexagonal classes One feature may be noticed When $\pi r/d$ is small the curves have almost the same form for all values of β *Therefore the reflexions of low order can be directly used to obtain the distances* r *of the atoms from the hexagonal axes*

The position of each typical silicon or oxygen atom in the projection on the c plane is defined by two parameters r γ The latter is the angle made by the radius on which the atom lies with a standard direction chosen for convenience to be CB shown in fig 5 below The intensities of a number of reflexions around the c zone were measured From these the corresponding F values were calculated using the values of extinction found as above The contributions of the aluminium and beryllium atoms F_1 and F_2 to these values of F are known since these atoms are in definite positions Subtracting the contributions one obtains a quantity $(F - F_1 - F_2)$ which must be accounted for by the silicon and oxygen atoms The ambiguity about the sign of F does not exist in practice because it is clear from the approximate structure what it should be The values F_{Si} and F_O for a single silicon and oxygen atom at a given glancing angle are taken fron Table IV and the required factor for the groups of six atoms read off from the curves in fig 4 for values of r and γ (β can be derived from γ by adding an angle depending on the inclination of the plane to CB) The contribution for small glancing angles depends almost entirely on r alone as has been pointed out Starting with these orders possible ranges of simultaneous values of the parameters r (Si) $r\,(O^{23})$ $r\,(O^{24})$ are found which give the correct algebraic sum of F contributions Each successive reflexion considered narrows these ranges until finally a set of parameters is found which gives a satisfactory fit for all spectra Various factors aid this analysis the F curve for oxygen falls away very quickly with increase of glancing angle so that the parameters of the silicon atom can be fixed accurately from the higher orders and also there are flat regions on some of the curves in fig 4 where the variation of a parameter produces little effect so that if the contributions of one set of atoms fall in this region various positions of the other atoms can be conveniently tested

The chief uncertainty lies in the F curves for aluminium beryllium, silicon and oxygen The agreement between calculated and observed values of F would no doubt be improved by a more accurate set of curves, but the positions assigned to the atom would not be greatly affected because a very small shift of an atom alters so rapidly its contribution to the higher orders

The values of the parameters finally chosen are given below both in the

(r, γ) form and as distances measured parallel to the sides of the unit cell The definite positions of the Be and Al atoms are included in the list Fig 5

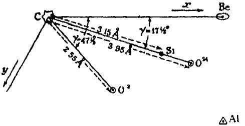


Fig 5 —Projection showing parameters (r, γ) of typical atoms projected on (0001)

illustrates the way in which the parameters are defined, z being measured away from the observer and from the origin at C

Table V

Atom	Number in unit cell	Co ordinates $r\gamma$ of typical atom		Co ordinates of position in unit cell					
				As fraction of unit translation			In Ångström units		
		r	γ				x	y	z
Al	4	—	—	$\frac{2}{3}$	$\frac{1}{3}$	0	6 14	3 07	0
Be	6	—	—	$\frac{1}{2}$	0	0	4 605	0	0
Si	12	3 15	17½°	0 39	0 12	$\frac{1}{4}$	3 55	1 09	2 29
O^{24}	24	3 95	17½°	0 48	0 15	0 10	4 45	1 37	0 94
O^{12}	12	2 55	47½°	0 30	0 24	$\frac{1}{4}$	2 81	2 17	2 29

The origin of co-ordinates has been chosen at the point where the horizontal twofold axes cut the c axis The co-ordinates may be referred to an origin at a centre of symmetry by adding $c/4$ to all z co-ordinates

In Table VI we give a complete list of the reflexions whose intensities have been measured, of the values of F calculated from these intensities by the formula for reflexion, and of the algebraic sums of the contribution to F made by atoms in the structure we have assigned to the crystal The two columns of F values show satisfactory agreement The uncertainty in values of F for the atoms at larger glancing angles explains discrepancies between the two columns for higher orders

Since numerical agreement between calculated and observed values of F for about thirty planes has been obtained by adjusting eight variables, consisting of seven parameters and the coefficient of extinction, the assigned structure is well confirmed

As an additional check values of F for a number of other planes have been calculated and compared with the maximum ionisation current observed when the crystal was set so as to reflect The results are given in Table VII In all cases a strong reflexion has corresponded to a large value of F and a weak reflexion to a small value of F The figures in column II are very approximate estimates of intensity and should be compared with the figures in column IV, to which they should be roughly proportional

Table VI

I	II	III	IV	V	VI
Indices	Sin θ	$\rho \times 10^6$	Intensity $\rho \times 10^6$ (Corrected for Extinction)	$\pm$ F (Calculated from IV)	F (for atoms in position of Table V)
(10$\bar{1}$0)	0 0387	95	206	67	−68
(11$\bar{2}$0)	0 0663	22	28	34	−40
(0002)	0 0669	160	478	137	139
(20$\bar{2}$0)	0 0774	38	56	50	−55
(30$\bar{3}$0)	0 1159	8 1	8 9	24	24
(22$\bar{4}$0)	0 1326	1 0	1 0	12	12
(0004)	0 1340	104	248	134	134
(40$\bar{4}$0)	0 1546	25 6	33 7	55	−50
(5050)	0 1935	39 6	58 6	82	87
(33$\bar{6}$0)	0 1999	14 5	17 5	45	−45
(0006)	0 2007	111	264	178	174
(60$\bar{6}$0)	0 2320	14 2	16 7	48	43
(44$\bar{8}$0)	0 2650	trace	—	—	−7
(0008)	0 2675	92	197	180	184
(70$\bar{7}$0)	0 2709	4 0	4 3	27	−20
(80$\bar{8}$0)	0 3094	16 9	20 4	63	60
(55 $\overline{10}$ 0)	0 3313	trace	—	—	14
(000 10)	0 3343	4 0	4 3	30	35
(90$\bar{9}$0)	0 3483	nil	—	—	4
(10 0 $\overline{10}$ 0)	0 3870	nil	—	—	−6
(66 $\overline{12}$ 0)	0 3995	17	20 6	76	78
(000 12)	0 4014	19	23 7	82	102
(77 $\overline{14}$ 0)	0 4641	nil	—	—	−3
(000 14)	0 4679	10	11 0	60	36
(88 $\overline{16}$ 0)	0 5300	nil	—	—	−1
(00016)	0 5350	3 5	3 7	40	56
(00018)	0 6021	nil			16
(00020)	0 6686	3 0	3 2	40	34

Table VII

I. Indices	II. Peak (maximum ionization current)	III F (calculated from structure)	IV $F^2\theta \times 10^{-4}$.
$(31\bar{4}0)$	33	30	6 8
$(62\bar{8}0)$	nil	12	0 46
$(21\bar{3}0)$	90	65	38
$(42\bar{6}0)$	53	70	23
$(41\bar{5}0)$	190	84	40
$(82\overline{10}0)$	nil	13	0 42
$(51\bar{6}0)$	10	19	1 7
$(22\bar{4}2)$	17	12	0 92
$(44\bar{8}4)$	32	30	2 7
$(66\overline{12}6)$	27	23	1 0
$(44\bar{8}2)$	120	61	10
$(31\bar{4}1)$	430	75	50
$(62\bar{8}2)$	130	65	13

7 *Fourier Analysis of Electron Distribution*.—A very elegant method of analysis has recently been developed by Duane and used by Havighurst. It was first suggested by W. H. Bragg in 1915,[*] though it could not then be directly applied to the determination of electron distribution because measurements of absolute intensities of reflexion were not available. If a set of crystal planes be considered, the distribution of diffracting matter in sheets parallel to the planes is a periodic function of the distance z, measured perpendicularly to the planes, which is repeated at intervals "d" equal to the spacing of the planes. Such a distribution can be represented by a Fourier series in the ordinary way. W. H. Bragg showed that the amplitude of reflexion by the planes for the first order of reflexion owed its existence to the first coefficient of the Fourier series, that of the second order to the second coefficient, and so on. Conversely, if the amplitude of reflexion in a number of orders is measured experimentally, a curve representing the electron distribution in sheets parallel to the planes can be built up by adding together the terms of the Fourier series. The idea underlying the method is precisely that used in Abbé's treatment of the resolving power of a microscope. The microscope is supposed to be focussed on a grating which is transmitting homogeneous light. Spectra are formed in a plane between the objective and the eyepiece, and these spectra in their turn act as sources of light and build up an image of the grating which is viewed by the eyepiece. The information as to the structure of the grating

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[*] W. H. Bragg, 'Phil. Trans. Roy Soc.,' A, vol 215, p. 253 (1915).

which the microscope gives depends on the number of spectra which the aperture of the objective allows to pass If the first three orders are formed for example an image of the grating will be seen which corresponds to the sum of the first three terms in a Fourier series, which, when complete would give the distribution of amplitude transmitted in passing from line to line of the grating The analogy between the X ray and optical problems is complete except in that it is possible to use the eyepiece to view the image formed in the microscope whereas in the case of X rays and a crystal it is only possible to measure the intensities of the spectra The summation of the Fourier series is carried out automatically in the image plane of the microscope but it has to be done by calculation in the second case

Duane* has put the necessary formulæ in a very simple form Havighurst† has used them in order to calculate the electron distribution in sodium chloride and other simple crystals basing his results on figures given by W L Bragg James and Bosanquet To use the method it is necessary to have measurements of the quantities we have termed F In order to get an accurate representation of the electron density values of F should be known for all orders up to a point where they become very small as compared with the lower orders

We are indebted to a private communication by Prof A H Compton of Chicago for the precise form in which the formula is quoted here Let the total number of electrons in the unit cell of volume V be Z The distribution of these electrons in sheets parallel to a given set of crystal planes with spacing *d* will be examined An area A on the planes will be chosen such that $Ad = V$ the volume of the unit cell containing Z electrons The number of electrons in the volume Adz is given by the expression

$$Z f(z)\, dz$$

where z is measured perpendicularly to the crystal planes and

$$\int_{d/2}^{d/2} f(z)\, dz = 1$$

It will in addition be supposed that the crystal has centres of symmetry This case is much more simple to treat than that of a crystal without such centres since it avoids the complication of difference of phase in the components of the Fourier series It can then be shown that

$$Z f(z) = \frac{Z}{d} + \frac{2F_1}{d} \cos \frac{2\pi z}{d} + \frac{2F_2}{d} \cos \frac{4\pi z}{d} + \quad + \frac{2F_n}{d} \cos \frac{2\pi n z}{d} + \qquad (5)$$

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* Duane Proc. Nat Acad Sci vol 11 8 p. 489 (1925)

† Havighurst, Proc Nat Acad Sci. vol. 11 8 pp. 502 and 507 (1925)

where F_1 F_2 F_n are the values of F calculated from the observed intensities of reflexion

Substituting the experimental values of F " in this formula a curve can be obtained which shows the electron distribution parallel to any given set of crystal planes In applying this to a crystal such as beryl due regard must be paid to the sign of F The experimental values of F are given in column V of Table VI and their signs may be got from the calculated values in column VI

The curves of figs 6 and 7 show the distribution of electron-density in sheets parallel to (0001) $(10\bar{1}0)$ $(11\bar{2}0)$ of beryl The curves are values of $Zf(z)$ calculated from formula (5) Since the curves are symmetrical it is only necessary to show one half of the complete repeat of the pattern in each case The (0001) spacing is halved and therefore the corresponding curve in fig 6 must be repeated four times in order to get the distribution between planes a distance 9 17 Å apart the length of the *c* axis (*cf* fig 2) In the other two cases one may suppose the curves reflected in the $Zf(z)$ axis so as to give the complete pattern The area within the square gives the scale of the figure in each case

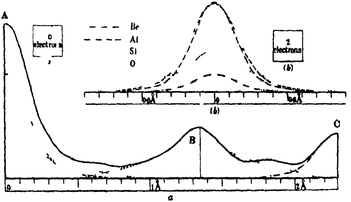

FIG 6

The structure of the (000*l*) planes is very simple and it is possible to analyse the curve so as to obtain an idea of the distribution of electrons in the various atoms The peak B in the middle of the curve is due to six oxygen atoms of the group $Be_6Al_4Si_{12}O_{36}$ The peak A on the left when completed by reflexion is due to six silicon atoms and six oxygen atoms Therefore, by subtracting from it the peak B one may obtain a curve representing the effect of the six silicon atoms alone. Some latitude is possible in choosing the exact form of the oxygen peak where the peaks A and B overlap, but it will be clear from the figure that there is not much choice, since the sum of the two oxygen curves cannot exceed the total height of the $Zf(z)$ ordinate at any point. Similarly, by subtracting that part of the oxygen curve which extends towards the peak C one obtains a curve for the distribution of electrons in the group Al_2Be_3. The complete distribution of electron density is made up of these four components, Si_6 and O_6 at A, O_6 at B, Al_2Be_3 at C. The components are shown as dotted curves in the figure.

The total area under the curve measures the number of electrons in the unit cell. This number is 532, and one quarter of these, 133, are represented by the area under the part of the curve in fig. 6A. Similarly, the areas under the dotted curves measure the number of electrons associated with Si_6, O_6, and Al_2Be_3. (It will be realised that the numbers of atoms will be in the right ratio for a molecule $Be_3Al_2Si_6O_{18}$ when the curve is repeated by reflexion.) These areas, as drawn in the figure, give the following numbers of electrons.

Si_6	74·8 electrons	12·47 electrons per atom
O_6	53·7 electrons	8·95 electrons per atom
Al_2Be_3	30·1 electrons	

The distribution of electrons amongst the silicon and oxygen atoms lies between that to be expected from neutral atoms, for which the value for silicon would be 14 and for oxygen 8, and that for ionized atoms, with values 10 and 10. Of course, the oxygen curve could be so drawn that the ratio 10 to 10 would exist, but if this is done trial shows that it is impossible to suppose the oxygen curve symmetrical on both sides of its peak. This may in fact be the case, since the oxygen atoms in peak B are united on one side to the silicon atoms in peak A to form a ring of the composition Si_6O_{18}. It seems simplest, however, to assume the oxygen curve symmetrical, and suppose that silicon and oxygen divide the electrons between them in the ratio of about 12·5 to 9. The point involved here is an interesting example of the power of Duane's direct method of analysis. We are not correct in speaking of the atoms as being in definite "positions" except when we may assume that the distribution of electrons around them is highly symmetrical.

The number of electrons in the aluminium and beryllium atoms separately cannot be deduced from the curve for Al_2Be_3 and we have arbitrarily split up this curve into two components of area corresponding to 11·4 and 2·4 electrons. In this way curves are obtained for the electron distribution in the atoms Be, Al, Si, O which are shown in fig. 6.

It is now possible to compare the experimental curves for the distribution of electrons in sheets parallel to the planes $(10\bar{1}0)$ and $(11\bar{2}0)$ given by the Fourier analysis with the distribution got by adding together the contributions from the various atoms. The positions of the atoms are fixed by the parameters of Table V, and the structure of the planes is indicated in fig. 7. As will be seen the comparison is not unfavourable. The Fourier series is not complete and the addition of higher terms might eliminate some of the chief differences between the two curves. In addition, the distributions for the various atoms deduced from the $(000l)$ planes may be incorrect. For instance, the fit would be improved if beryllium were given more electrons and aluminium fewer.

The method of Fourier analysis proposed by Duane may well prove to be a more simple and direct method of finding structures than the method usually followed, in which atomic arrangements are assumed and their effects compared with experiment. Duane's method has the supreme merit of presenting in the form of a single curve the information yielded by *all* orders of reflexion from a given plane. One can imagine it possible to take the curves of electron distribution in the various atoms, and by sliding them along the z axis in a way conformable with symmetry to obtain the best possible fit to the observed Fourier curve and so to analyse the structure. In the simple case of the $(000l)$ planes, for example, the displacement of the oxygen atoms parallel to the c axis is immediately read off from the curve instead of being deduced from a number of orders. It is interesting to note that the peak of the curve in fig. 6 is at a distance from the Si_6O_6 planes, which agrees within 1 per cent. of the distance 1·35 A deduced from the spectra. It must be remembered, however, that an extinction coefficient has been chosen which makes calculated and observed intensities agree for the $(000l)$ planes so that the Fourier analysis should here give the same results as ordinary analysis.

Though this method may be more direct, it depends like other methods on accurate measurements of the quantity we have called "F." If "F" is known for a large number of planes, analysis will be possible by one method or another. In its turn, "F" depends on the estimation of the effect of extinction. All other factors can be allowed for, and the experimental measurements of intensity present no difficulties. *Accurate allowance for extinction appears to be the key to the analysis of complex structures.*

Whatever method of analysis is finally adopted it seems necessary to work out an approximate structure in the first place. The Duane method cannot be

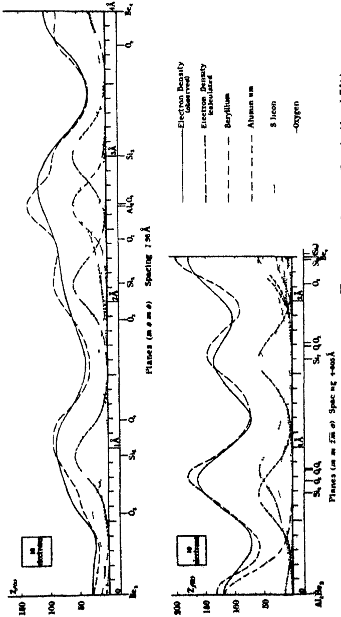

FIG 7.—Fourier Analysis of Planes (m o m̄ o) and (m m 2̄m o) in Beryl   *Correction* $Z_{f(z)}$ should read $Zf(z)$.

applied until the signs of the coefficient F are fixed by preliminary analysis, for the observed intensities only give the squares of these quantities Probably the most convenient procedure will be to combine the trial and error method of assuming structures and calculating the spectra to be expected from them with the Fourier analysis method the latter being used to make the final adjustments of atomic position and to indicate the accuracy of the results

8 *Discussion of the Structure*—In the beryl structure every silicon atom is surrounded by four oxygen atoms arranged tetrahedrally every aluminium atom by six oxygen atoms at the corners of an octahedron and every beryllium atom by four oxygen atoms on a distorted tetrahedron The silicon and oxygen atoms form rings of the composition Si_6O_{18} These rings have a hexagonal axis and equatorial plane of symmetry and are arranged around the hexagonal axes They are composed of SiO_4 groups each group joined to its neighbour on either side in the ring by an oxygen atom held in common The rings are stacked on each other along the hexagonal axes forming a series of open channels, for no atomic centre is nearer than 2 55 Å to a hexagonal axis The rings are linked together by the aluminium and beryllium atoms as shown in fig 3 The whole structure is like a honeycomb, with the hexagonal axes passing down the centres of the cells and with walls formed of closely packed oxygen atoms The open channels in the structure parallel to the c axis are very striking and suggest investigations into properties they might confer on the crystal

Table VIII—*Interatomic Distances*

Si Group	$O^{12} - O^{24}$	= 2 54 Å
	$O^{24} - O^{24}$	= 2 70 Å
	$O^{12} - O^{12}$	= 2 55 Å
	$Si - O^{24}$	= 1 57 Å
	$Si - O^{12}$	= 1 58 Å
Al Group	$O^{24} - O^{24}$ (parallel to (0001))	= 2 93 Å
	$O^{24} - O^{24}$ (common to Be group)	= 2 52 Å
	$O^{24} - O^{24}$ (parallel to $(10\bar{1}0)$)	= 2 54 Å
	$Al - O^{24}$	= 1 94 Å
Be Group	$O^{24} - O^{24}$ (parallel to (0001))	= 2 91 Å
	$O^{24} - O^{24}$ (parallel to $(10\bar{1}0)$)	= 2 52 Å
	$O^{24} - O^{24}$ (parallel to $(11\bar{2}0)$)	= 3 03 Å
	$Be - O^{24}$	= 1 73 Å

The groups of oxygen atoms around Be Al and Si are similar to the groups in garnet, $Ca_3Al_2Si_3O_{12}$, analysed by Menzer In garnet each calcium atom is surrounded by four oxygen atoms each aluminium by six oxygen atoms and each silicon by four oxygen atoms In both crystals the distances between oxygen atoms are everywhere about 2 7 A The distances between neighbouring atoms in beryl are given in Table VIII

In conclusion we wish to express our gratitude to Dr A Hutchinson F R S for providing us with crystal specimens Part of the apparatus used in the investigation was presented to the laboratory by the General Electric Company of America

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Structure in the Secondary Hydrogen Spectrum—IV

By O W RICHARDSON F R S Yarrow Research Professor of the Royal Society

(Received June 1 1926.)

§ 1 *Fulcher's Bands*

Fulcher's bands as extended by himself[*] and Allen [†] consisted of six sets of five lines in the red whose wave numbers obey a parabolic law very closely both when the lines within each set are compared and when corresponding lines in each set are compared from set to set There were also four sets of four lines in the green with similar properties The numerical coherence of these lines has been ably discussed by Curtis [‡] and I have nothing to add to that discussion except to say that on plates taken by Mr Wilfred Hall with a 21 foot grating the line λ — 6127 40 (16315 64ν) is shown resolved with one component which preliminary measures place at λ = 6127 21 the value suggested by Fulcher It thus appears that the anomaly in this line is due to blending and not to a perturbation

In addition to the foregoing lines Fulcher included four other lines in the first four sets in the red which he denoted by the letters S_4 S_5 S_6 S_7 These lines follow the parabolic law from set to set, but their interrelation within each set is far from obvious An attempt to include them in a consistent scheme has been made by Dieke [§] who arranges the vertical series of Allen (S_3, S_2, S_1 S_0, S_{-1})

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[*] Fulcher Phys. Rev vol. 21 p 375 (1923)

[†] Allen, Roy Soc Proc A vol 106 p 69 (1924)

[‡] Curtis, Roy Soc Proc A vol 107 p 579 (1925)

[§] Dieke, Proc. Kon. Akad v Wet Amsterdam, vol 27 p 490 (1924).

as the first five lines of Q branches of which S_6 is the seventh line whilst S_4 and S_7 are the first and second line respectively of associated R branches There are serious objections to the arrangement proposed for the lines S_4—S_7 although I shall show that there is strong evidence for the correctness of the arrangement of Allen s vertical series as Q branches In the first place Dieke s scheme has no place for any of the S lines nor for the S_6 lines 5989 22 6093 83 and 6399 45 whereas the credentials of S seem as good as those of S_4 or S_6 and one S_6 line seems as good as another or at least the physical evidence for a connection between the S_6 lines and the S_2-S_1 lines is no better for those which are included than for those which are excluded In the second place an examination of the numerical coherence of the wave numbers of the lines in the R series proposed by Dieke shows that it is too irregular for this arrangement to be likely to be correct

A good deal of light is thrown on this problem by an examination of the spectrum of hydrogen in the first type discharge * The electrical conditions in this discharge are especially favourable to the production of excited H_2 molecules and relatively unfavourable to the production of other possible emitters It is likely therefore that the spectrum observed under these conditions is that of the neutral H_2 molecule In this discharge the strength in the red consists almost entirely of H_α and Fulcher s lines This is well shown by figs 1 and 2 These are two microphotometric prints taken for me on a Moll and Burger instrument by Adam Hilger Ltd from prismatic spectrograms on panchromatic plates of the region from H_α to beyond 5537 45 A U the leading line of the third Fulcher triplet in the green Fig 1 which is for an ordinary Geissler tube discharge shows a mass of lines with a maximum average of

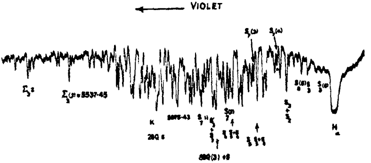

FIG 1 —Geissler Tube Discharge.

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* *Cf* Richardson and Tanaka Roy Soc Proc A vol 106 p 640 (1924)

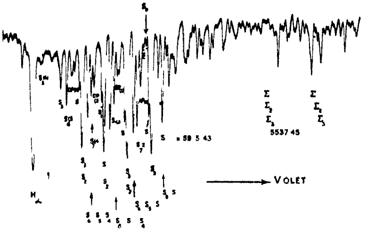

Fig 2 First Type Discharge

intensity in the neighbourhood of 6000 Å U and with no obvious regularity of structure Fig 2 is a spectrogram of the luminosity of the first-type discharge under similar dispersion It will be seen that the strength on the violet side of 5975 43 Å U has almost entirely disappeared The only recognisable structure remaining is that of the green Fulcher bands and the lines in the neighbourhood of 5700 Å U which have recently been arranged by Curtis * Between 5975 43 Å U and H_α on the other hand the red Fulcher bands stand out with great strength some of the lines being comparable in intensity with H_α The strength coming from other systems which makes the intensity distribution in the Geissler tube discharge (fig 1) so irregular is here suppressed and the pattern consists of repeating units of the lines S_7 $S_6 + S_5 + S_4$ (unresolved) $S_3 + S_2$ (unresolved) and S_1 The first four units are very distinct but the two last nearest H_α are fading out In addition to these lines S_0 and S_{-1} can be recognised in the first unit and the four lines AP (2) = 6067 70 Å U BP (2) = 6169 63 Å U CP (2) = 6271 31 Å U and DP (2) = 6372 19 Å U clearly belong to the same system These additional lines have not been given by Fulcher A very similar development of intensity distribution to that of fig 2 is also shown by a plate taken at a low pressure at − 252° C which was kindly lent to me by Prof J C MacLennan † The low pressure low temperature and low voltage electron excitation features of this spectrum make it necessary that the strong lines in

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* Curtis Phil Mag. vol 1 p 695 (1926)

† *Cf* MacLennan and Shrum Trans Roy Soc Canada vol 18, p 177 (1924)

for example fig 2 should be those which belong to low rotational quantum numbers of the system The lines of higher rotational quantum numbers if they exist must be weaker lines The problem of the red Fulcher bands thus narrows itself down to the discovery of suitable additional lines which will enable the $S_1 - S_7$ lines and the added P (2) line to form the low rotation quantum number lines of a band unit This problem I propose to solve in the manner shown by fig 3 This represents the band unit in the red system which is

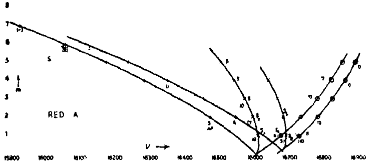

Fig 3

nearest the violet and is denoted by the letter A the others proceeding towards H_α being denoted by the letters B C D E and F in succession Following Allen and Dieke I use the lines S_3 S_2 S_1 S_0 and S_{-1} as a Q branch AQ (*m*) $m = 1$ 2 3 4 5 S_4 and P (2) I use as the leading lines AR (1) and AP (2) of R and P branches corresponding to AQ (*m*) It will be shown that weaker lines exist to form a reasonable number of additional members The lines S_6 and S_5 I use as the two leading lines of a new Q branch and denote them by AQ^1 (1) and AQ^1 (2) Here again suitable coherent weaker lines can be found and it will be shown that there is an important parallelism between the various Q (*m*) and Q^1 (*m*) branches in respect to their response to helium excitation The last line S_7 I use as the leading line of an R branch AR^1 (1) associated with AQ^1 (*m*) Weaker lines to continue this and also lines for an associated P branch AP^1 (*m*) can be found A corresponding arrangement has been found for the B C D and E sets in the red but the last set has become too attenuated for anything but FQ (*m*) to be discoverable with certainty although there are lines which might be FQ^1 (1) FQ^1 (3) and FQ^1 (4) Branches corresponding to AP (*m*) Q (*m*) R (*m*) as far as DP (*m*) Q (*m*) R (*m*) have been found in the green and as far as EP (*m*), Q (*m*), R (*m*) in the blue A combination principle holds between each set of bands and the others

§ 2 *The New Q Series in the Red*

Table I

	Properties								I W in Air (Int)	Wave Number	1st Diff	2nd Diff
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
									AQ (*m*)			
1	+ +		+				S_4	3	5989 22 (5)	16692 04	7 52	9 44
2			+				S_5	abs	5991 92 (2)	16684 52	16 96	7 71
3			+ +	+				1	5998 02 (2)	16667 56	24 67	
4			+	+				0	6006 91 (3)	16642 89		
									BQ¹ (*m*)			
1			+				S_6	abs	6093 83 (2)	16405 52	5 73	10 66
2		+ +					S_5	7	6095 96 (8)	16399 79	16 39	7 82
3								abs	6102 05 (0)	16383 40	24 21	
4				+ +				*	6111 08 ( )	16359 10		
									CQ¹ (*m*)			
1	+ +						S_4	abs	6197 05 (5)	16132 25	6 05	10 27
2		+ +					S_5	"	6199 38 (9)	16126 20	16 32	
3								abs.	6206 66 (*q*)	16109 88		
									DQ¹ (*m*)			
1		+ +					S_6	5	6299 42 (7)	15870 09	7 18	9 75
2			+				S_5	abs	6302 27 (2)	15862 91	16 93	7 35
3								abs	6309 01 (0)	15845 98	24 28	
4							IV a0Q(3)	0	6318 65 (1)	15821 80		
									EQ¹ (*m*)			
1		+ +					S_6	5	6390 45 (6)	15622 02	11 11	7 79
2							FR (1)	abs	6404 01 (1)	15610 91	18 90	
3				()			DP (3)	0	6411 77 (1)	15592 01	59 28	
3									missing			
5								abs	6436 24 (*qd*)	15532 73		
									FQ¹ (*m*)			
1								0†	6499 87 (0)	15380 09	(12)	(5 2)
2										(15368 7)	(17 2)	(7 0–)
3								abs	6512 22 (0)	15351 53	24 22	
4							? FQ (0)	abs	6532 50 (0)	15327 31		

* Doubtful if present

† Mixed with 6497 88 (0)

The properties in this and similar tables are as set forth in Merton and Barratt's Tables and as used in my previous papers except for column 8, which exhibits estimates of the relative intensities of the lines on a plate of the first type discharge. It will be observed that with this discharge the alternation in intensity of the lines of any Q^1 branch is more marked than that given by Merton and Barratt's intensities which are for a discharge of the Geissler tube type but with a low current density, and the same is true, though to a less degree, of the intensities of the lines in the various Q branches. The extreme weakening of the relatively strong S_8 line 6197·05 (5) = C^1Q (1) is very striking. It may have to do with the high pressure character of the line, but AQ^1 (1) which is also a high pressure line, is not similarly affected. An examination of C^1Q (1) on Mr Hall's plate, with a pocket microscope, shows no evidence of duplicity. The fact that the weakened lines are those for m even in A, D and E and for m odd in B and CQ^1 (m) may be significant.

The differences in the wave numbers of the lines are quite coherent, although the second differences are not constant. So far as the vertical differences are concerned this is shown by fig 4, in which × indicates first differences and ○

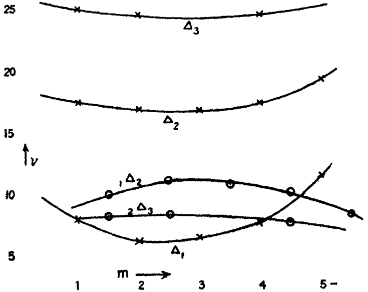

FIG. 4

indicates second differences plotted against m. The horizontal first and second differences are shown in Table II.

Table II

m	A (m	B (n)	——	C¹(n)	—	D¹(m)	—	E¹(m)
1	286 52		73 27		262 16	——	248 07	
		13 25		11 11		14 00		
2	284 73	——	273 59		263 29	——	252 00	
		11 14		10 30		11 29		
3	284 16	——	273 52		263 90	——	253 97	
		10 64		9 62		9 93		
4	283)							

The third vertical second difference is probably about 0 3 cm^{-1} too low at 10 27 Otherwise all the lines are coherent to within the accuracy of measurement and there is no evidence of perturbations The only evidence of the occurrence of blends lies in the fact that lines $DQ^1(4)$ $FQ^1(2)$ and $EQ^1(3)$ are claimed by other series as IVa0Q (3)* FR (1) and DP (3) (see below) respectively

Important further evidence of the reality of the $Q^1(m)$ branches is derived from a comparison of the effect of helium on these lines and on the $Q(m)$ lines This gas has a peculiar and selective effect on the $Q(m)$ lines a fact to which my attention was drawn independently by Prof Merton and by Dr Curtis In the $AQ(m)$ branch helium depresses the line Q (1) has little effect on Q (2) slightly enhances Q (3) strongly enhances Q (4) and very strongly enhances Q (5) so much so that on a helium plate this line is stronger than Q (2) Broadly the effect is a weakening of the low rotation quantum lines and a strengthening of the high rotation quantum lines A similar phenomenon takes place in $BQ(m)$ $CQ(m)$ and $DQ(m)$ except that the low quantum weakening effect tends to increase and the high quantum strengthening effect to diminish as we proceed from $BQ(m)$ towards $DQ(m)$ Now the interesting thing in the present connection is that a precisely parallel phenomenon is found in the corresponding Q^1 branches This will be clear from Table III which exhibits the relative intensities of the various lines of the Q and Q^1 branches on a H_2 + He plate and a comparison H_2 plate for which I am indebted to Prof Merton

The numbers given in Table III are visual estimates from the appearance of the lines of the intensities on the usual conventional scale and have no absolute meaning but they suffice to establish the close parallelism referred to It may perhaps be permissible to add that these lines were originally picked out from the numerical requirements set by the S_3 and S_5 lines without any knowledge either of the strengthening of the alternating character by the first type discharge or of the helium phenomena, and no alterations were subsequently made in the list

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* Sandeman Roy Soc Proc A vol 110 p 326 (1926)

Table III

He effect on Q (*m*) branches

Line	No He		He
AQ (1)	10	→	10 –
AQ (2)	7	—→	7
AQ (3)	10	→	10 +
AQ (4)	2+	→	6
AQ (5)	2+	→	8
AQ (6) 16464 48 [ ]	abs	→	2+
BQ (1)	10	—→	5
BQ (2)	8	→	6
BQ (3)	10	→	7
BQ (4)	3	→	1
BQ (5)	4	→	3
CQ (1)	10	→	2
CQ (2)	7	→	2
CQ (3)	9	→	2
CQ (4)	3	→	1
CQ (5)	4	→	1
DQ (1)	8	→	1
DQ (2)	5	→	9
DQ (3)	8		1
DQ (4)	1	→	abs
DQ (5)	3–	→	1+
EQ (1)	6		1
EQ (2)	2	→	? abs
EQ (3)	4	→	? abs
EQ (4)	0	→	abs
EQ (5)	0	→	abs
FQ (1)	4	→	abs
FQ (2)	1		abs
FQ (3)	2	—→	abs

He effect on Q¹ (*m*) branches

Line	No He		He
AQ¹ (1)	5		2
AQ¹ (2)	3+		1
AQ¹ (3)	2	→	3
AQ¹ (4)	3	→	7
BQ¹ (1)	2		2
BQ¹ (2)	9		8
BQ¹ (3)	0	—→	0
BQ¹ (4)	abs		2
CQ¹ (1)*	6		4
CQ¹ (2)	8	→	5
CQ¹ (3)	9	→	abs
DQ¹ (1)	8	→	1
DQ¹ (2)	4		0
DQ¹ (3)	9		abs
DQ¹ (4)	1	→	abs
EQ¹ (1)	6	→	1–
EQ¹ (2)	1		abs
FQ¹ (3)†	1	—→	1
EQ¹ (5)	d	—→	abs

* Not completely resolved from 6197 72

† The exceptional behaviour of this line may be accounted for by the fact that it is also claimed as DP (3)

§ 3 *The P and R Branches in the Red*

Table IV

	Properties								W L in Air (Int)	Wave Number	1st Diff	2nd Diff
									AR (*m*)			
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1		++	=	O		S_1		4	5994 05 (6)	16678 59	55 65	8 30
2			+	O				*	5974 12 (3)	16734 24	47 35	8 68
3						AR¹ (2)		<0	5957 26 (0)	16781 59	38 67	6 54
4			++					abs	5943 57 (2)	16820 26	32 13	
5			+					abs	†5932 24 (2)	16852 39		

* Probably absent

† Double on Hall s plates

Table IV—continued

Properties									W L in Air (Int)	Wave Number	1st Diff	2nd Diff
					BR (*m*)							
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1		++				S_4		7	6098 23 (6)	16393 66		
2	++		++					2	6074 39 (4)	16458 01	64 35	
3	+		++			IVa81 (6)		4	6053 27 (4)	16515 44	57 43	6 92
4						* 1571 (1)		abs	6035 02 (0)	16565 38	49 94	7 49
					CR (*m*)							
1		++	=			δ		?abs	6201 15 (5)	16121 59		
2			+					3*	6176 88 (2)	16190 19	68 60	
3			+					1†	6151 47 (4)	16251 79	61 60	7 00
4			+					<0	6131 83 (2)	16303 85	52 06	9 54
5								abs	6115 60 (0)	16347 11	43 26	8 80
					DR (*m*)							
1		++	=			S_4		1	6303 46 (3)	15859 93		
2	++		+					<1	6274 86 (5)	15932 22	72 29	
3							CQ (4) 157P (5)	1	6249 15 (3)	15997 74	65 52	6 77
4												
5												
								?	6207 31 (1)	16105 60		
					ER (*m*)							
1						EQ¹ (3)		abs.	6404 01 (1)	15610 91		
2								abs.	6374·11 (0)	15679 21	68 30	

* Mixed with 6176 18 (3) = 1P(7) + 157P(3)

† Mixed with 6158 17 (3)

Table IV (continued)

AP (*m*)

	Properties								Wl in Air (Int)	Wave Number	1st Diff	2nd Diff
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
2	++					3P (2) 158R (2)		5*	†6067 70 (5)	16476 14	87 63	
3			++					abs	6100 18 (1)	16388 42	100 74	13 12
4	+							abs	6137 91 (1)	16287 68	108 81	8 07
5								abs	6179 19 (0)	16178 87	118 56	9 75
6		+ +	=			S3 (3) 1Vo7(P2) 157P (4)		8	6224 81 (9)	16060 31	131 45	12 89
7				++				1	6276 18 [ ]	15928 86		

* Mixed with 6070 00 (7) = 83Q (2) † Double on Hall's plate

BP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Wl in Air (Int)	Wave Number	1st Diff	2nd Diff
2		+ +	+					3	†6169 63 (5)	16203 96	94 08	
3								abs	6205 66 (*g*)	16109 88	105 06	11 58
4			+	O		157I (6)		abs	†6246 63 (2)	16004 22	114 91	9 23
5								0	6291 80 (0)	15889 31	122 21	7 30
6		+				S_1 (4)		2	†6340 57 (6)	15767 10	129 27	7 06
7				+				abs	6392 99 [ ]	15637 83		

† Double on Hall's plate

CP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Wl in Air (Int)	Wave Number	1st Diff	2nd Diff
2		++						2	6271 31 (3)	15941 24	100 48	
3								abs	6311 09 (*g*)	15840 76	112 28	11 80
4								?	6356 14 (0)	15728 48	121 72	9 44
5								abs	6405 71 (0)	15606 76		

DP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Wl in Air (Int)	Wave Number	1st Diff	2nd Diff
2		+						1	6372 19 (3)	15688 85	96 84	
3				O		EQ¹ (3)		0	6411 77 (1)	15592 01	107 08	10 24
4								0	6456 11 (0)	15484 93	109 35	2 27
†5								abs	6502 03 (1)	15375 58		

FP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Wl in Air (Int)	Wave Number	1st Diff	2nd Diff
2								0	6472 24 (*p*)	15446 35	91 82	
3								abs	6512 22 (0)	15351 53		

The first lines of each branch are low pressure lines which are depressed by the condensed discharge The two lines AP (2) and BP (2) which form an exception to this statement are both found to be double under higher resolution The later members tend to come up in the condensed discharge and the two first P branches (A and B) show a similar property to the corresponding Q and Q^1 branches of enhancement by helium for the highest rotation quantum numbers It is not pretended that the strong lines 6224 81 (9) = CQ (1) and 6340 57 (6) = DQ (3) belong here They merely cover up places where members are to be expected but the faint companion of DQ (3) (S_1 (4)) might be BP (6) The differences are all quite regular if some slight allowance is made for the known doublets The lines claimed by other series which have not yet been found to be double all involve weak interferences which may be difficult of detection It should be remarked in connection with the numbers in column 8 which represent intensities on a plate of the first type discharge that the luminosity in this discharge is very weak and the absence of lines which are of intensity (1) or less in the ordinary Geissler tube discharge has little significance The points which they seem to establish are (1) an alternating intensity in the R branches (particularly noticeable in the strongest branch BE (*m*)) (2) the strongest lines are for *m* odd except possibly in CR (*m*) for which branch the plate is difficult to interpret and (3) the first lines (*m* = 2) of the P branches are definitely present on the plate with a reasonable diminution in intensity from AP (2) to EP (2)

The horizontal first and second differences of the red R (*m*) and the red P (*m*) lines are exhibited in the following table —

Table V

Red R (*m*)

m		A (*m*)	——	B (*m*)	——	C (*m*)	——	D (*m*)	——	E (*m*)
1	(1st)		284 93		272 07		261 66	——	249 02	
	(2nd)			12 86		10 41		12 64		
2	(1st)		276 23	——	267 82	——	257 97	——	243 37	
	(2nd)			8 41		9 85		14 60		
3	(1st)		266 15	——	263 65	——	254 05	——	246 44	
	(2nd)			2 50		9 60		7 61		
4	(1st)		254 88	——	261 53					
	(2nd)			6 65						

Red P (*m*)

m		A (*m*)	——	B (*m*)	——	C (*m*)	——	D (*m*)	——	E (*m*)
2	(1st)		272 18	——	262 72	——	252 39	——	242 50	
	(2nd)			9 46		10 33		9 89		
3	(1st)		278 54	——	269 12	——	248 75	——	240 48	
	(2nd)			9 42		20 37		8 27		
4	(1st)		283 46	——	275 74	——	243 55			
	(2nd)			7 72		32 19				
5	(1st)		289 56	——	282 55					
	(2nd)			7 01						
6.	(1st)		293 21							
	(2nd)									
7	(1st)		291 03							
	(2nd)									

Both the vertical and horizontal differences seem quite regular At any rate there is no irregularity beyond what might be expected as a result of the interferences shown in Table IV

§ 4 *The* P¹ *and* R¹ *Branches in the Red*

Table VI

	Properties								W L in Air (Int)	Wave Number	1st Diff	2nd Diff
AR^1 (*m*)												
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1		++	--	0		S_7		8	5975 43 (10)	16730 59		
											51 01	
2						AR (3)		<0	5957 26 (0)	16781 60		7 73
											43 26	
3			++					2	5941 95 (1)	16824 83		7 97
											35 29	
4				+				abs	5929 52 (0)	16860 14		6 83
											28 44	
? 5								abs	5919 73 (0)	16888 58		
BR^1 (*m*)												
1		++				S_7		9	6080 78 (9)	16440 52		
											67 21	
2		+		++		S_1 (1)		abs	6056 10 (5)	16507 73		9 56
											(57 65)	
3						157P (1)		abs	6035 02 (0)	16565 38		(7 50)
											(50 15)	
4							calculated line			(16615 53)		(7 45)
											(42 70)	
5								abs	6001 38 (*p*)	16658 23		
CR^1 (*m*)												
1		++	=			S_7		6	6182 98 (8)	16168 96		
											71 89	
2								2	6155 01 (5)	16240 85		8 89
											63 00	
3			+			CR (4)		? 0*	6131 83 (2)	16303 85		7 66
											55 34	
? 4				++		BQ^1 (4)		abs	6111 08 [ ]	16359 19		

* The wave length of the line on the plate seems low

DR^1 (*m*)												
1		++				S_7		4	6285 37 (6)	15905 58		
											70 49	
2								0	6257 63 (0)	15976 07		7 33
											63 16	
3								abs	6232 99 (4)	16039 23		
ER^1 (*m*)												
1								<1	6391 04 (6)	15642 50		
											70 19	
2								3	6362 48 (5)	15712 79		7 02
											63 17	
3								abs	6337 01 (0)	15775 96		8 03
											55 14	
4						BP^4 (6)		1–	6316 0– (–)	15831 1–		

Table VII

	Properties								W L in Air (Int.)	Wave Number	1st Diff	2nd Diff
									AP^1 (*m*)			
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
2	+		+					2	6041 01 (4)	16548 95	90 94	
3			+ +				BR (2)	2	6074 39 (4)	16458 01	103 42	12 48
4				+				1	6112 80 (0)	16354 59	113 74	10 32
5								<2*	6155 61 (5)	16240 85	122 45	8 71
6								abs	[6202 4 [ ]	16118 4		
									BP^1 (? ?)			
2								1	6153 17 (3)	16247 30	98 90	
3			new	line				1	6190 9	16148 4	109 17	10 27
4							DR^1 (3)	abs	6232 99 (4)	16039 23	119 67	10 50
5							?1P (8)	abs	6279 85 (0)	15919 56		
									CP^1 (*m*)			
2							BP^3 (5)	abs	6264 89 (0)	15957 57	104 18	
3							?159Q (3)	abs.	6306 06 (0)	15853 39	112 88	8 70
4							S_6 (4)	abs	6351 28 (1)	15 40 51		
									DP^1 (*m*)			
2								abs	6376 11 (0)	15679 21	99 66	
3			new	line				0	6417 0—	15579 55	111 24	11 58
4							EP^1 (1)	abs	6463 05 (*pd*)	15468 31		
									EP^1 (*m*)			
2							EP^4 (3) ?163P (6)	abs	6487 76 (0)	15409 39	87 08	
3?								abs	6534 63 [ ]	15322 31		

* Mixed with 6153 17 (2) ?

The P^1 branches cannot be regarded as so certainly established as the P branches since the lines are weak and the leading lines do not stand out on the plate as the P (2) lines do The number of lines available in the spectrum of the first-type discharge is, however, very limited, and it is doubtful if any alternative arrangement could be constructed which uses lines with any strength in this spectrum for the low rotation quantum numbers of the A and B branches If these branches are present, either AP (2) or AP (3) and either BP (2) or BP (3) ought to show up, even if the other lines are absent and it is satisfactory that such strength as the lines show in the first-type discharge is in the right place The two new lines assigned to BP^1 (3) and DP^1 (3) are present in the first type discharge, but are not given in Merton and Barratt s or Tanaka's tables They do not appear to be attributable to Hg N O C, Ca, Ba Cu, Al or Na so presumably they belong to hydrogen It should be added that no lines due to impurities have been found on the plates on which these lines occur The horizontal differences of R^1 (*m*) and P^1 (*m*) are shown in Tables VIII and IX

Table VIII —Horizontal Differences of Red R^1 (*m*)

m		A^1 (*m*)		B^1 (*m*)		C^1 (*m*)		D^1 (*m*)		E^1 (*m*)
1	(1st)		290 06	——	271 56	——	263 38	——	262 98	
	(2nd)			+18 50		+8 18		+0 40		
2	(1st)		273 86	— —	266 88	——	264 78	——	263 28	
	(2nd)			+6 98		+2 10		+2 50		
3	(1st)		259 47	——	261 53	——	264 62	——	263 27	
	(2nd)			−2 06		−3 09		+1 35		
4	(1st)		(244 81)	——	(256 34)					
	(2nd)			(11 73)						
5	(1st)		230 35							

$CR^1(4) - ER^1(4) = 528\ 09$
$= 2 \times 264\ 05$

Table IX —Horizontal Differences of Red P^1 (*m*)

2	(1st)		301 65		289 73		278 36		269 82	
	(2nd)			11 92		11 37		12 58		
3	(1st)		309 61		295 01		273 84		257 24	
	(2nd)			14 60		21 17		16 60		
4	(1st)		315 36		298 72		272 20			
	(2nd)			16 64		26 52				
5	(1st)		321 29							

All these numbers seem coherent The three numbers in brackets involve the interpolated wave number 16615 53 used for BR^1 (4) Tables VI and VII show a considerable number of interferences which may be difficult to settle It may be pointed out, however, that the claims of 1 P (8), 159 Q (3) and 163 P (6) to the three relevant lines in the P^1 (*m*) branches are very slight With one exception all the other lines are lines which function twice in the Fulcher band system as now extended

§ 5 *The Bands in the Green*

The lines of the Q branches and their properties etc are shown in Table X The main lines are the same as those given by Fulcher but some weak extensions have been added which it does not seem possible definitely to exclude at present The more rapid diminution of intensity of the higher rotation quantum lines in the first type discharge is very evident and on Prof MacLennan s plate at – 252° C there is practically nothing left except the first line of each band The tendency of the high quantum lines in the A band to come up in helium is very marked just as it was in the two red Q branches As in the red the green R branches are weaker but the lowest quantum lines show a definite persistence possibly amounting to enhancement in some cases in the first type discharge and on the low temperature plate The property of coming up in helium at the end of the branch seems now to have moved from the A branch to the others Again as in the red the P branches are still weaker than the R branches but the important lines BP (2) and CP (3) of the two strongest bands persist both in the first type discharge and at – 252° C It is, of course difficult to be sure of the fainter lines in these weak branches and the lines given for AP (4) AR (3) and AR (5) might be replaced collectively by 18516 80 (3) 19011 48 (0) (= 53 P (6)) and 19065 01 (1) without much detriment to the numerical relationships Considering the character of this spectrum the number of suspected interferences in the green bands is not high

Table X —Green Q (*m*)

	Properties								W L in Air (Int)	Wave Number	1st Diff	2nd Diff
									AQ (*m*)			
m.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1				O				5	5303 15 (8)	18851 49		
											20 87	
2			–					1	‡5309 03 (4)	18830 62		10 53
											31 40	
3	++			O				abs	5317 90 (5)	18799 22		10 39
											41 79	
4	+			+			27 P (3)	0*	5329 74 (1)	18757 43		9 19
											50 98	
5				++				1†	5344 27 [–]	18706 45		9 57
											60 55	
†6				++			BR (4)	abs	5361 63 [ ]	18645 90		9 09
											69 64	
7				++				abs.	5381 72 [ ]	18576 26		

* Mixed with 5326 80 (2) † Mixed with 5343 19 (2) ‡ Unresolved doublet (M and B.)

Table X—(continued)

BQ (*m*)

Properties									W L in Air (Int.)	Wave Number	1st Diff	2nd Diff
m	(1)	(2)	x(3)	(4)	(5)	(6)	(7)	(8)				
1		++						6	5419 90 (6)	188445 52		
											20 69	
2								4	5425 96 (3)	*18424 83		9 42
											30 11	
3								3	5434 83 (5)	18394 72		9 95
											40 06	
4				+				abs	5446 70 (0)	18354 66		9 67
											49 73	
5			+					1	5461 50 (1)	18304 93		9 40
											59 13	
6								abs	[5479 2– –]	18245 8–		8 42
											67 55	
?7		++	++					1	5499 56 (2)	18178 25		5 91
											73 46	
?8			+				152 R (7)	abs	5521 87 (0)	18104 79		1 10
											74 56	
?9			+	O				?	5544 70 (0)	18030 23		

* Double under high resolution

CQ (*m*)

m	(1)	(2)	x(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int.)	Wave Number	1st Diff	2nd Diff
1		++						6	5537 45 (7)	18053 86		
											19 44	
2		+	+	O				2	5543 41 (2)	*18034 42		10 43
											29 57	
3			+					1	5552 52 (4)	18004 85		9 28
											38 85	
4			++				83 Q (8)	0	5564 53 (2)	17966 00		9 27
											48 12	
5			+					0	5579 47 (0)	17917 88		

* Unresolved doublet (M and B)

DQ (*m*)

m	(1)	(2)	x(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int.)	Wave Number	1st Diff	2nd Diff
1		+	−					4	5655 75 (5)	17676 22		
											18 64	
2			−					1	5661 72 (3)	17657 58		9 91
											28 55	
3								<1	5670 89 (3)	17629 03		9 15
											37 70	
4			++				G (5)	abs	*5683 05 (2)	17591 33		12 17
											49 87	
5							164 Q (4)	abs	5699 20 (0)	17541 46		

* Double under high resolution; the fainter component is about ¼ Å.U towards the violet.

Table XI —Green R (*m*)

	Properties								W L in Air (Int.)	Wave Number	1st Diff	2nd Diff
					AR (*m*)							
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1								2*	5283 30 (2)	18922 30		
											46 30	
2	++			+				abs	5270 41 (3)	18968 60		7 65
											38 65	
3								abs	5259 69 (0)	19007 25		4 12
											34 53	
4							53 P (6)	abs	5250 15 (0)	19041 78		6 61
											27 92	
5								1†	5242 46 (*p*)	19069 70		

* Mixed with 5284 50 (4) = 18917 98 (?185P (6)) † Recorded on first type measures as 5241 14 (broad)

BR (*m*)

1		+						2	5401 06 (1)	18509 75		
											53 49	
2		++	−					abs	5385 50 (3)	18563 24		8 45
											45 04	
3								1	5372 46 (0)	18608 28		7 42
											37 62	
4				++				abs	5361 63 [1]	18645 90		

CR (*m*)

1		++						1	5518 48 (2)	18115 91		
											62 34	
2		++	++					1	5499 56 (2)	18178 25		10 45
											51 89	
3								abs	5483 90 (0)*	18230 14		6 14
											45 75	
4				++			AP (6)	0†	5470 17 [–]	18275 89		

* Measured on one plate only (M. and B) † Diffuse on first-type plate

DR (*m*)

1								1*	5634 31 (0)†	17743 49		
											57 07	
2			+				169 Q (1)	abs	5616 24 (0)	17800 56		10 72
											46 35	
3				++			157 Q (7)	abs	5601 66 (0)	17846 91		9 2
											37 09	
† 4								abs	5590 04 (*q*)	17884 00		

* Probably mixed with 5634 78 recorded as broad on first-type plate
† The band line might be 17742 02 = 5634 78 (3)

Table 12 —Green P (*m*)

AP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L. in Air (Int)	Wave Number	1st Diff	2nd Diff
2			—				162 R (5)	abs	5340 84 (1)	18716 46		
											96 39	
3								abs	5368 48 (*qd*)	18622 07		11 96
											108 35	
4			++				27 P (4)	abs	5399 90 (0)	18513 72		6 28
											114 63	
5								abs	5433 54 (*q*)	18399 09		8 57
											123 20	
? 6				++			CR (4)	0*	5470 17 [ ]	18275 89		

* Diffuse on first-type plate

BP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L. in Air (Int)	Wave Number	1st Diff	2nd Diff
2			+					1	5456 97 (1)	18320 12		
											105 17	
3				++				abs	5488 48 [ ]	18214 95		12 00
											117 17	
4								abs	5524 01 (0)	18097 78		

CP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L. in Air (Int)	Wave Number	1st Diff	2nd Diff
2							186 R (5)	0	5573 86 (1)	17935 93		
											105 53	
? 3								abs	[5606 8— —]	17830 4—		18 5
											124 —	
4								0*	5646 12 (0)†	17706 39		5 —
											129 —	
5								abs	5687 56 (*q*)	17577 35		

† Measured on one plate only (M and B)
* Measured on first-type plate as 5644 99 (broad)

DP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L. in Air (Int)	Wave Number	1st Diff	2nd Diff
2	+		++	O			K (4)	4	*5689 19 (7)	17572 81		
											113 53	
3			++				201 R (3)	abs	5725 87 (1)	17458 78		9 96
											123 49	
4			++					(1)	5766 98 (2)	17335 29		12 44
											135 93	
5	++		++	++	Z		Kı (1) 23 Q (3)	6	*5812 56 (9)	17199 36		

* The band lines may be absent The strength in both cases belongs to other systems

The horizontal first and second differences for the green R and P branches are shown in Table XIII The corresponding differences for the Q branches have been tabulated by Curtis * The figures in brackets involve the substitute 17826 4—) for the line 17830 4—[—] given in the table of properties This takes the irregularity out of both vertical and horizontal differences

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* *Loc cit*

Table XIII —Horizontal Differences

Green R (*m*)

m		A (*m*)	——	B (*m*)	——	C (*m*)	—	D (*m*)
1	(1st)		412 55	——	393 84	——	372 42	
	(2nd)			+18 71		+21 42		
2	(1st)		405 36	——	384 99	——	377 49	
	(2nd)			+20 37		+7 50		
3	(1st)		398 97	——	378 14	——	383 23	
	(2nd)			+20 83		−0 09		
4	(1st)		395 88	——	370 01	——	391 89	
	(2nd)			+25 87		21 88		

Green P (*m*)

m		A (*m*)	——	B (*m*)	——	C (*m*)	—	D (*m*)
2	(1st)		398 34	——	384 19	——	363 62	
	(2nd)			+14 15		+20 57		
3	(1st)		407 12	——	(388 55)	——	(367 62)	
	(2nd)			+(18 57)		+(20 93)		
4	(1st)		415 94	——	391 39	——	371 10	
	(2nd)			+24 55		+20 29		
5	(1st)						377 99	

§ 6 *The Bands in the Blue*

(1) *The Q Branches* —That a number of lines exist in the blue which are closely related to the Fulcher lines in the red and green was first recognised by Gehrcke and Lau* from observations of the spectrum of hydrogen excited by slowly moving electrons A considerable number of these were arranged by Dieke† in Q branches similar to those already proposed for the red and green Q branches Table XIV shows Dieke s arrangement of these lines with the addition of three lines which are underlined once, and the substitution of three lines, underlined twice for other lines given by Dieke I have also adjusted the wave numbers of two lines which are abnormally strong (CQ (3) and DQ (2)), this takes out the irregularity in the vertical differences One of these lines is abnormal in showing the Zeeman effect and is given by Merton and Barratt as a high pressure line It is probably a blend As regards the interferences, 83 R (*m*) and 10 P (*m*) are both rather doubtful single branches the line denoted as AQ (1) is expressly mentioned as a doubtful member of his band by Sandeman,‡ and the line denoted as AQ (6) does not appear on his plates Although the lines of Fulcher's bands do not show the Zeeman effect, the Zeeman property of AQ (1) might be genuine, as Curtis and Jevons§ have found that the first line of a branch in the helium

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* Gehrcke and Lau. Berlin Akad Sitzber Jahrg.,' p. 453 (1922); p 242 (1923)

† *Loc. cit.*

‡ *Loc cit*

§ Curtis and Jevons, 'Nature (1925)

band spectrum will sometimes show this effect when the other lines do not The intensity and its distribution among the lines in the first-type discharge and at − 252° C is very strong evidence in favour of the reality of these bands The line DQ (2) = 4683 79 is abnormal both in intensity and wave number and might be perturbed It behaves both in the first type discharge and at low temperature as though it belonged to the band The AQ branch in the blue is distinguished by the same susceptibility to helium stimulation as the AQ branches in the green and the red but in the blue band it is not confined to the lines of high rotational quantum number but extends to every line in the branch A peculiarity of the blue Q branches is that the line for which $m = 4$ is extremely weak or absent in every branch Both in the blue and in the red and green Q branches there is an alternation of intensity with the weakness in the lines for which m is even If lines having the wave numbers given in Table XIV are used for the two missing lines BQ (4) CQ (4) it will be seen from Table XV that there are no irregularities either in the horizontal or in the vertical differences

Table XIV Blue Q (m)

	Properties								W L in Air (Int.)	Wave Number	1st Diff	2nd Diff
					AQ (m)							
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1		++		++	Z		SaQ (9) 8	6	4490 45 (5)	22263 24	15 95	
2		++		++				2	4493 67 (2)	22247 29	23 98	8 03
3				+	O		85 Q (5)	8*	4498 52 (2)	22223 31	31 47	7 49
4		++		++				0	4504 90 [ ]	22191 84	38 88	7 41
5				++			? 83 R (6)	a	4512 81 (1)	22152 96	46 82	7 94
6				++			SaR (6)	? †	4522 37 (0)	22106 14		
					BQ (m)							
1		++						7	4554 13 (4)	21951 97	15 36	
2		++						3	4557 37 (2)	21936 61	23 65	8 29
3								3	4562 24 (2)	21912 96	(31 66)	(8 01)
4										(21881 3)	(40 14)	(8 48)
5							10 P (1) BP (2)	a	*4577 23 (0)	21841 16		

* Weak if present Mixed with 4498 10 (6) † Very weak if present.

* Measured on one plate only (M and B.).

Table XIV—continued

	Properties								W L in Air (Int)	Wave Number	1st Diff	2nd Diff.
									CQ (*m*)			
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1		++	=					7	4617 49 (3)	21650 73		
											15 12	
2		+					BP (4)	4	4620 72 (1)	21635 61		7 48
											22 60	
3	++			O	Z			4	4625 39 (4)	†21613 01		(7 91)
											(30 51)	
4										(21582 5-)		(8 79)
											(39 30)	
5				++				0	4640 47 [ ]	21543 20		
											48 27	
6								0*	4650 96 (*x*)	21494 93		

* Mixed with 4650 34 (0)
(*x*) line measured by Tanaka and described by him as of quite variable intensity
† *Wave number of line reduced 0 75 cm* ¹ *to take out irregularity*

DQ (*m*)

1		++						3	4680 43 (2)	21369 92		
											14 86	
2		+			O			6	4683 79 (5)	*21344 76		6 75
											21 61	
3								0	4688 43 (0)	21323 15		

* Wave number of line increased by 0 50 cm ¹ to take out irregularity

EQ (*m*)

1		++						6	4742 75 (3)	21078 95		
											14 47	
2								1	4745 94 (*p*)	21064 78		6 53
											20 70	
3								2*	4750 61 (*p*)	21044 08		

* Mixed with 4751 59 (1)

Table XV —Blue Q (*m*) Horizontal Differences

m		AQ (*m*)	—	BQ (*m*)	—	CQ (*m*)	—	DQ (*m*)	—	EQ (*m*)
1	(1st)		311 27	—	301 24	—	291 11	—	280 67	
	(2nd)			10 03		10 13		10 44		
2.	(1st)		310 68	—	301 00	—	290 85	—	279 98	
	(2nd)			9 68		10 15		10 87		
3	(1st)		310 35	—	299 95	—	289 86	—	279 07	
	(2nd)			10 40		10 09		10 79		
4	(1st)		(310 54)		(298 80)					
	(2nd)			(11 74)						
5.	(1st)		311 80		297 96					
	(2nd)			13 84						

(2) *The R and P Branches* —As in the red and green these branches are much weaker than the Q branches and are more difficult to locate with certainty owing

to the fact that they are mixed up with some other systems which are strong in the first-type discharge In fact, a microphotograph of the first type in this region, whilst exhibiting considerable strength between H_β and H_γ shows little or no regularity of the type shown in fig 2 by the Fulcher bands in the red The lines given in Tables XV and XVI under A and B are the lines which I

Table XV —Blue R (*m*)

AR (*m*)

	Properties								W L in Air (Int)	Wave Number	1st Diff	2nd Diff
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1	+			++	Z		26 P (4) S	2	4474 24 (2)	22343 92		
											50 64	
2				++			61 Q (3)	0	4464 12 (1)	†22394 56		8 18
											42 46	
3		+		O				2	4455 67 (1)	22437 02		10 95
											31 51	
4								3*	4449 42‡(*p*)	22468 53		10 35
											21 16	
5					Z		3 M (3) S	5	4445 24 (3)	22489 69		

* Mixed with 4449 92 (1) = 85Q (4)
† Unresolved doublet (M and B)
‡ Not completely resolved from 4451 34 (Tanaka)

BR (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int)	Wave Number	1st Diff	2nd Diff
1								0	4537 83 (1)	22031 28		
											62 26	
2								*	4524 95 (*r*)	22093 54		10 01
											52 25	
3	+			++	O		SaQ (8)	1	4514 27 (1)	22145 79		6 20
											46 05	
4		++		++			AQ (4) 3 M (5)	0	4504 90 [-]	22191 84		

* *Weak if present*

C_2R (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int)	Wave Number	1st Diff	2nd Diff
1	+			+			111 P (5)	0	4605 35 (0)	21707 79		
											63 91	
2							5 M (2)	1	4591 84 (1)	21771 70		7 84
											56 07	
3		++		+	O		SaP (5) ? AR (5)	7	4580 04 (5)	21827 77		12 39
											43 68	
4							CR (3)	abs.	4570 89(*rd*)	21871 45		

D_2R (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int)	Wave Number	1st Diff	2nd Diff
1		++						1	4667 80 (1)	21417 40		
											45 83	
2	+							1	4657 83 (1)	21463 23		11 26
											34 57	
3								0	4650 34 (0)	21497 80		17 09
											17 48	
4							BP (5)	abs	4646 56 (0)	21515 28		

Table XV- (contanued)

E_2R (*m*)

m.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L. in Air (Int)	Wave Number	1st Diff	2nd Diff
1		+						1	4732 81 (1)	21133 20		
											29 85	
2								abs	4726 12 (0)	21153 05		9 38
											20 47	
3								0	4721 56 (1)	21173 52		9 08
											11 39	
? 4					Z			7	4719 02 (6)	21184 91		

Table XVI —Blue P (*m*)

AP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int).	Wave Number	1st Diff	2nd Diff
2	+			++			101 R (4) S	0	4515 47 (1)	22139 91		
											91 34	
3				++				*	4534 17 (3)	22048 57		13 55
											104 89	
4								abs	4555 87 (*r*)	21943 68		11 02
											115 91	
5		++		+	O		SaP (5)	7	4580 04 (5)	21827 77		13 63
											129 54	
6	++			++	Z		101 R (2)	2	4607 38 (3)	21698 23		

* Probably absent, but may be mixed with 4534 56 (3) = SQa (7), which has strength (4) on first type plate.

BP (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int).	Wave Number	1st Diff	2nd Diff
2							BQ (5) 10 P (1)	abs.	4577 23 (0)*	21841 16		
											94 94	
3		++						2	4597 22 (1)	21746 22		15 67
											110 61	
4		+					CQ (2)	4	4620 72 (1)	21635 61		9 72
											120 33	
? 5							DR (4)	abs	4646 56 (0)	21515 28		

* Measured on one plate only (M. and B.)

C_2P (*m*)

m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	W L in Air (Int).	Wave Number	1st Diff	2nd Diff
2								0	4643 83*(*p*)	21537 92		
											107 08	
3	+				Z		56 R (5)	abs	4667 05 (1)	21430 84		7 02
											114 10	
4					Z		56 R (4)	1	4692 04 (2)	21306 74		19 12
											133 22	
5								0	4721 56 (1)	21173 52		

* Probably identical with 4643 83 [ ] in Merton and Barratt's Tables (Tanaka).

Table XVI—(continued)

	Properties								W l in A r (Int)	Wave Number	1st Diff	2nd Diff
									D_2P (*m*)			
m	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
2								0	4705 24 (0)	21 46 53		
											123 33	
3		+						1	4732 81 (1)	21123 20		14 17
											137 50	
4		++			O		185 R (2) S	5	4763 82 (4)	20985 70		16 34
											153 84	
5								abs	4799 00 (0)	20831 86		
									E_2P (*m*)			
2								abs	4769 50 (0)	20960 72		
											134 33	
3								abs	4800 26 (*r*)	20826 39		8 08
											143 31	
4								abs	4833 52 (*q*)	20683 08		9 18
											152 49	
? 5							38 R (2) 58 R (3)	2	4869 42 (2)	20530 59		

believe to be the AR (*m*) BR (*m*) AP (*m*) and BP (*m*) branches corresponding to the branches with the same notation in the red and green but a large proportion of the lines are claimed by other series Unfortunately the rival claimants mostly belong to systems which also exhibit considerable strength in the first type discharge and at low temperature so that it is not possible to distinguish the band lines satisfactorily by the methods previously employed Of the interferences 10 P (1) and 38 R (2) belong to branches of doubtful authenticity but there is something to be said for each of the others The number of interferences seems to exceed what is reasonable purely as a result of the operation of chance so that perhaps some of the higher quantum lines ought to be taken out of this table However it seems as well to include them until this part of the spectrum has been investigated under higher resolution

The lines given under C_2 D_2 and E_2 seem fairly definite branches which show the usual behaviour in the first type discharge and at low temperature but they are not coherent with the A and B lines This can be seen from the vertical differences in the tables and is just as evident in the horizontal differences There are however a number of lines in this region which can be arranged coherently with the A and B lines as fragments of P and R branches corresponding to the C D and EQ branches These are given in Table XVII Their coherence with the A and B lines is shown by the vertical differences in Table XVII and also by the horizontal differences in Table XVIII

Table XVII —Blue R (*m*) and P (*m*)

	Properties								W L in Air (Int)	Wave Number	1st Diff	2nd Diff
							CR (*m*)					
m.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)				
1								0*	4600 06 (*r*)	21732 75		
											73 88	
2		++						3	4584 48 (1)	21806 63		9 06
											64 82	
3							C_2R (4)	abs	4570 89 (*rd*)	21871 45		5 34
											59 48	
4				+	Z		101R (3) 26P (5)	3	4558 50 (2)†	21930 93		
	* May be mixed with 4600 81 (*r*)								† Unresolved doublet (M and B)			
							CP (*m*)					
2							60R (5) 20P (7)	0	4638 58 (0)	21552 28		
											93 37	
3								1*	4658 79 (*p*)	21458 91		
							* Mixed with 4657 83 (1).					
							DR (*m*)					
1		++			O			5*	4661 30 (4)	21446 85		
											86 36	
2				++				abs	4642 69 [ ]	21533 21		13 04
											73 32	
3								?	4626 94 (0)	21606 53		
	* May be mixed with 4660 34 (3)								? = very weak if present			
							DP (*m*)					
2								abs	4698 21 (*rd*)	21278 99 = *(21275 72)		
							* Value required by combination principle					
							ER (*m*)					
1								0	4721 56 (1)	21173 52		
											97 51	
2								abs	4699 92 (*pd*)	21271 03		17 72
											79 79	
3								1	4682 35 (3)	21350 82		—1 67
											81 46	
4								abs	4664 56 (*q*)	21432 28		
							EP (*m*)					
2			—					0*	4758 39 (0)	21009 64		
											(65 78)	
3								abs		‡(20943 86)		18 06
											(83 84)	
4			—					abs	4792 52 (0)	20860 02		—0 84
											83 00	
5								0†	4811 67 (0)	20777 02		

* Mixed with 4760 06 (0) † May be mixed with 4810 54 (*p*)

‡ Value got by combination principle.

Table XVIII —Horizontal Differences

Blue R (*m*)

m		AR (*m*)		BR (*m*)		CR (*m*)		DR (*m*)		ER (*m*)
1	(1st)		312 64	——	298 53	——	285 90	——	273 33	
	(2nd)			14 11		12 63		12 57		
2	(1st)		301 02	——	286 91	——	273 42	——	262 18	
	(2nd)			14 11		13 49		11 24		
3	(1st)		291 23	——	274 34	——	264 92	——	255 71	
	(2nd)			16 89		9 42		9 21		
4	(1st)		276 69	——	260 91					
	(2nd)			15 87						

Blue P (*m*)

m		AR (*m*)		BR (*m*)		CR (*m*)		DR (*m*)		ER (*m*)
2	(1st)		298 75	——	288 88	——	276 56*	——	266 08*	
	(2nd)			9 78		12 32*		10 48*		
3	(1st)		302 35	——	287 31					
	(2nd)			15 04						
4	(1st)		308 07							
	(2nd)									
5	(1st)		312 49							

* These numbers involve the use of the line (21275 72) which is got from DR (1) by the combination principle instead of the line 21278 77 (*rd*) which is probably double as DP (2)

In forming a final judgment as to the reality of these blue R and P series, it should be borne in mind that all the lines in Tables XV–XVII to which it is applicable satisfy the combination principle subject to a reasonable allowance of errors due to interferences or possibly wrong lines Another point in their favour is that the P branches are weaker than the R branches, and the R than the Q just as is the case in the green and red bands

§ 7 *The Combination Principle*

The lines of all the foregoing R and P branches (but not of the R^1 and P^1 branches) satisfy a combination rule such that $R(m) - P(m+1)$ for any given value of *m* has a certain value for all the A bands, a certain other value for all the B bands, and so on, irrespective of whether the bands concerned are in the red, the green or the blue group This is shown by the data in Table XIX This table includes some data got from a blue C_1 band, the details of which have been taken out of this paper for further consideration The P and R branches of this band do not belong to the same Q branch as the others

The values of $P(m) - R(m)$ for the lines of the red, green and blue groups are given in Table XX The corresponding values for the green and blue do not satisfy a combination rule, but they run in a similar way to those in the red Table XXI gives the values of the red $R^1(m) - P^1(m+1)$ and Table XXII those of the red $R^1(m) - P^1(m)$ There is some fragmentary evidence of a second P^1 branch in the red and of branches in the green whose lines satisfy a combination rule similar to that for the R (*m*), P (*m*) lines, but I do not propose to produce it now, as it has not yet been sufficiently examined

Table XIX —Values of R (*m*) — P (*m* + 1) and their next differences

	m →	1		2		3		4		5
A	*red*	202 45*		345 82		493 91		641 39		792 08
	green	203 84		346 53*		492 53		642 69		789 12* or 793 81*
	blue	204 01		345 99		493 34		640 76		791 46
	means	203 93		345 91		493 59		641 61		791 77
			141 98		147 68		148 02		150 16	
B	*red*	189 70		348 13		511 22		676 07		
	green	189 63		348 29		510 86				
	blue	190 12		347 32*		510 18*		676 56		
	means	189 82		348 21		511 04		676 32		
			158 39		162 83		165 28			
C	*red*	180 35		349 43*		523 31		697 09		
	green	179 98		347 35		523 75		698 54		
	blue C_1	180 20		347 87		523 38		698 27*		
	blue C_2	179 87		350 86*		521 03*		697 93		
	blue C	180 47		347 72						
	means	180 17		347 65		523 48		697 85		
			167 48		175 83		174 37			
D	*red*	171 08		340 21		512 81				
	green	171 18		341 78*		511 62		684 64 ?		
	blue D_2	170 87		340 03		512 10		683 42 ?		
	means	171 04		340 12		512 18		684 03		
			170 08		172 06		171 85			
E	*red*	164 56		327 68						
	blue E_2	162 48*		326 66		490 44		654 32 ?		
	blue E	163 88				490 80		655 26 ?		
	means	164 22		327 17		490 62		654 79		
			162 95		163 45		164 17			

* These lines which involve either interferences or doubtful lines have been disregarded in taking the means

The numbers in Tables XIX–XXII are very interesting They represent coherent functions of the rotation quantum numbers *m* and of a set of consecutive integral numbers which might be assigned to the successive letters A, B, C, D, E, F It is probable that these letters correspond to different vibrational transitions $n \rightarrow n^1$, possible values being the diagonal transitions A = 0 → 0, B = 1 → 1 C = 2 → 2 D = 3 → 3 E = 4 → 4 and F = 5 → 5, and that the groups in the red, green and blue correspond respectively to different electron jumps* of the type considered in the elementary theory of line

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* This particular assumption is very doubtful It seems at least as probable that these groups correspond respectively to the alternative sets of vibrational transitions such as 1 ⟶ 0 2 ⟶ 1 3 ⟶ 2, and so on.

Table XX —Values of R (*m*) — P (*m*) and their differences

m →	2		3		4		5	
				Red				
A	258 10		393 17		532 58		673 52	
		135 07		139 41		140 94		
B	254 05		405 56		561 16			
		151 51		155 60				
C	248 95		411 03		575 37		740 35	
		162 08		164 34		164 98		
D	243 37		405 73				730 02 ?	
		162 36		324 29 (= 2 × 162 15)				
E	232 86		*					* ER (3) does not exist
				Green				
A	250 14		385 18		528 06		670 61	
		135 04		142 88		142 55		
B	243 12		393 33		548 12			
		150 21		154 79				
C	242 32		(403 74)		569 50			The numbers in brackets involve the substitute line (17826 4—) for CP (3)
		(161 42)		(165 76)				
D	228 25		388 13		548 71			
		159 88		160 58				
				Blue				
A	254 65		388 45		524 85		661 92	
		133 80		136 40		137 07		
B	252 38		399 57		556 23			
		147 19		156 66				
C	254 35		412 54					
		158 19						
D	†(257 49)							† These numbers use the values (21275 72) for DP (2) and (20942 86) for EP (3) got from the other lines by the combination principle
E	261 39		†(406 96)		572 26			
		†(145 57)		†(165 30)				
C_2	243 78		406 93		564 71			
		163 15		157 78				
D_2	216 70		374 60		529 58			
		157 90		154 98				
E_2	192 33		347 13		501 83 ?			
		154 80		154 70 ?				

spectra This interpretation is not absolutely certain but it is the simplest which is consistent with the facts and it seems desirable to adopt it until some reason for modification presents itself The numbers under any given letter such as A etc in any given colour, such as red etc will then represent the different rotation quantum jumps for the same vibrational quantum jump and the same electron orbital jump Successive differences, such as $R(m) - P(m+1)$ represent sequences of successive rotational energy terms or com

Table XXI —Values of the red $R^1(m) - P^1(m+1)$ and their differences

$m \rightarrow$	1		2		3		4		5	
A	181 63		323 58		470 26		619 29		770 18	
		141 95		146 68		149 03		150 89		
B	193 22		359 33		526 15		(695 97)*			* These numbers in brackets involve a calculated line $BR^1(4) =$ (16615 53)
		166 11		166 72		(169 82)*				
C	211 39		387 46		563 34					
		176 07		175 88						
D	226 37		396 52		570 92					
		170 15		174 40						
E	233 21		390 48							
		157 27								

Table XXII —Values of the red $R^1(m) - P^1(m)$ and their differences

$m \rightarrow$	2		3		4		5	
A	232 64		366 84		505 55		647 73 ?	
		134 20		138 71		142 18		
B	260 43		416 98		(576 30)*		738 67	* These numbers in brackets involve the calculated line $BR^1(4) =$ (16615 53).
		156 55		(159 32)*		(162 37)*		
C	283 28		450 46		618 68			
		167 18		168 22				
D	296 86		459 68					
		162 82						
E	303 40		453 65 ?					
		150 25						

binations of such sequences Their next differences do not vary much with m for any assigned letter and colour, but they are not constant and it is very doubtful if the precise manner of their variation with m can be accounted for on any theory which has been advanced up to the present To obtain a preliminary survey of the data I enquire what would be the result of assuming that each set of values of $\mathrm{R}(m) - \mathrm{P}(m+1)$ etc in Tables XIX XXII for any given sequence of m represents an integral sequence of successive differences of initial or final rotation terms I assume further that each of these hypothetical terms is represented by the expression $\mathrm{F}(m) = \mathrm{B}(m - e)^2$ where B and e are constants B and e cannot really both be constants as the next differences of $\mathrm{R}(m) - \mathrm{P}(m+1)$, etc, vary with m, but I avoid this difficulty by using only the first two terms ($m = 1$ and $m = 2$) in each case that is to say, I use only the data given by the lines R (1), R (2), R (3), P (2) and P (3) These assumptions are only defended on the ground that it is necessary to make a start somehow, but the lines used have the advantage that those with higher quantum numbers (m) tend to become less certain On these assumptions the provisional values of (2 B) and (e) are given in Table XXIII, and the values of (e) are plotted in fig 5

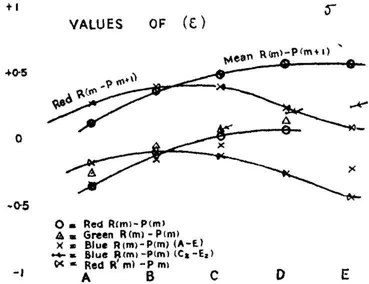

Fig 5

On the face of it the values of (2 B) all increase to a maximum in proceeding from A towards E and then fall again The value of e from R (m) − P (m + 1) starts near zero at A and approaches the value ½ asymptotically at E Similarly

Table XXIII —Values of 2 B and of e

	A	B	C	D	E
(1) From red green and blue R (m) − P (m + 1) (Means)					
2B →	141 98	158 39	167 48	170 08	162 95
e →	+0 0637	+0 3017	+0 424	+0 5001	+0 493
(2) From red R (m) − P (m)					
2B →	135 07	1 1 51	162 08	162 36	
e →	−0 410	−0 1767	−0 03595	+0 00105	
(3) From green R (m) − P (m)					
2B →	135 04	150 21	161 42	159 88	
e	−0 353	−0 1183	0 00118	+0 0723	
(4) From blue R (m) − P (m) (A → E)					
2B →	133 80	147 19	158 19		145 57
e →	−0 404	−0 2143	−0 108		0 296
(5) From blue R (m) − P (m) (C_2 D_2 E_2)					
2B →			163 15	157 90	144 80
e →			+0 00583	+0 1277	+0 172
(6) From red R^1 (m) − P^1 (m + 1)					
2R →	141 95	166 11	176 07	170 15	157 27
e	+0 222	+0 337	+0 330	+0 170	+0 0171
(7) From red R^1 (m) − P^1 (m)					
2B →	134 20	156 55	167 18	162 82	150 25
e →	−0 2335	−0 1635	−0 1943	−0 3236	−0 519

the red R (m) − P (m) starts near −½ and approaches asymptotically to zero The same behaviour is shown by the green and the blue R (m) − P (m) except that the green E and blue D are absent and the blue E is exceptional It may be that there are wrong lines in the blue E fragment, the failure of the D band makes them uncertain On the other hand there may be a perturbation here so that it is necessary to leave the matter undecided for the present The (e) values from the red $R^1(m) - P^1(m+1)$ start near $+\frac{1}{2}$ for A rise to a maximum and then fall to zero at E Similarly those from the red $R^1(m) - P^1(m)$ start near $-\frac{1}{2}$ at A rise to a maximum and fall to $-\frac{1}{2}$ at E

It may be that these changes in (2 B) and (e) correspond respectively to changes with vibration states in the moment of inertia and in the component of angular momentum perpendicular to the line joining the nuclei of the emitting systems But this is not certain and an alternative interpretation will be considered later There are however *some facts* in the data plotted in fig 4 which I feel must in any event be significant particularly the way in which as the state E is approached the value of (e) approaches one or other of the values 0 or $\pm\frac{1}{2}$ This becomes more significant when we remember (Tables XIX and XX) that for the $R(m) - P(m+1)$ and the red $R(m) - P(m)$ values the next differences have become practically constant at D and E and are equal to the difference $R(1) - P(2)$ multiplied by either 1 or $\frac{1}{2}$ This shows that the formula $B(m - e)^2$ with B and *e really constants* does apply at this end of these bands The parallelism of the curves in fig 4 and the fact that they always keep almost exactly half a quantum apart is also very striking

The $R(m) - P(m+1)$ terms are the same for the red the green and the blue bands This means that all these bands involve one common state either initial or final I shall assume it to be the final state the alternative being improbable I take it then that the $R(m) - P(m+1)$ terms represent the terms or some of them of this common final state I assume tentatively that the initial and final terms are of the form $B(m - E)^2$ where B and E are constants at least at the F F end of the bands Subject to these assumptions we have quite generally

$$R(m) = \nu_0 + B_1(m + 1 - E_1)^2 - b_1(m - e_1)^2 \quad m + 1 \longrightarrow m \tag{1}$$

$$P(m+1) = \nu_0 + B_2(m + 1 - E_2)^2 - b_2(m + 2 - e_2)^2 \quad m + 1 \longrightarrow m + 2 \tag{2}$$

Since $R(m) - P(m+1)$ have a common value for the differently coloured bands for the various values of m m and if the common terms are to be the final ones (distinguished by small letters) we must have identically

$$B_1(m + 1 - E_1)^2 \equiv B_2(m + 1 - E_2)^2$$

This requires that $B_1 \equiv B_2$ and $m' = m - E_1 + E_2$ Putting x for $E_1 - E_2 + e_2$ the fact that $R(1) - P(2) \sim R(2) - P(3) - [R(1) - P(2)]$ requires that $x - 2 = \pm e_1$ The solution $x - 2 = + e$ is rejected because it leads to $P(m+1) \simeq R(m)$, thus

$$x + e_1 = E_1 - E_2 + e_2 + e_1 = +2 \tag{3}$$

In a similar manner the fact that

$$R(2) - P(2) \simeq \tfrac{1}{2}\{R(3) - P(3) - [R(2) - P(2)]\},$$

in conjunction with $(x-2)^2 = e_1{}^2$ requires that

$$E_1 + E_2 = e_1 + e_2 \tag{4}$$

So that from (3)

$$E_1 = +1 \text{ and } e_2 + e_1 - E_2 = +1 \tag{5}$$

If the common terms are to be the final terms, then $m = m'$ with the numeration adopted in the tables, and there seems to be no reasonable alternative enumeration, so that

$$E_1 = E_2 = +1, e_1 + e_2 = +2 \tag{6}$$

Reasonable alternative sets of values satisfying (6) are

$$E_1 = E_2 = e_1 = e_2 = +1 \quad \text{or} \quad E_1 = E_2 = +1, \quad e_1 = +\tfrac{1}{2},$$
$$e_2 = +1\tfrac{1}{2} \quad \text{or} \quad E_1 = E_2 = +1, \quad e_1 = +1\tfrac{1}{2}, \quad e_2 = +\tfrac{1}{2}$$

So far as I can see at present, there is nothing in the evidence to hand which would make any of these three alternatives preferable to the others

For the P′ R′ branches I assume

$$R'(m) = \nu_0 + B'_1(m + 1 - E'_1)^2 - b'_1(m - e'_1)^2, m + 1 \longrightarrow m \tag{7}$$

and
$$P'(m+1) = \nu'_0 + B'_2(m + 1 - E'_2)^2 - b'_2(m + 2 - e'_2)^2, \tag{8}$$
$$m + 1 \longrightarrow m + 2$$

The combinations are not known but B'_1 B'_2 b'_1 b'_2 are not very different in magnitude, and since

$$R'(1) - P'(2) \simeq \tfrac{1}{2}\{R'(2) - P'(3) - [R'(1) - P'(2)]\}$$

it follows that

$$(E'_2 - E'_1)(1 - E'_2 + E'_1) = e'_1(e'_1 + 1) - (e'_2 - 2)(e'_2 - 1). \tag{9}$$

From the fact that

$$R'(2) - P'(2) \simeq 2\{R'(3) - P'(3) - [R'(2) - P'(2)]\}$$
$$(1 + E'_2 - E'_1)(1 - E'_2 + E'_1) = e'^2_1 - e'^2_2 + 2e'_2 - 1 \tag{10}$$

whence

$$E'_1 + E'_2 = e'_1 + e_2 \qquad (11)$$

and

$$(e'_1 + e'_2 - 1)(1 + e'_1 - E'_1) = 0 \qquad (12)$$

This requires that either

$$e'_1 + 1 = E_1 \qquad (13)$$

or

$$e_1 + e_2 = 1 \qquad (14)$$

If (13) were true, the formula for $R(m)$ would become

$$R(m) = \nu_0 + (B'_1 - b'_1)(m - e_1)^2$$

which would represent a Q branch not an R branch The alternative (14) is therefore adopted and also, from (11)

$$E'_1 + E_2 = 1 \qquad (15)$$

Even if we are confined to integers and half integers between -1 and $+2$, there are a considerable number of sets of values of $E_1\ E_2\ e'_1\ e'_2$ which satisfy (14) and (15) However, many of them are ruled out by the fact that the differences of $R(m) - P(m+1)$ are very nearly the same as those of $R'(m) - P'(m+1)$ Disregarding the differences between B_1 b_1, etc this common difference is $\Delta = 2B(2 - E_1 + E_2 + e_1 - e_2)$ The sets which satisfy this requirement (in the order $E_1\ E_2\ e_1\ e_2$) are —(*a*) for P, R = 1 1, 1, 1, P′, R′ = either 0, 1, 0 1 or 1 0, 1 0 or $-\frac{1}{2}$ $1\frac{1}{2}$ $-\frac{1}{2}$, $1\frac{1}{2}$ or $1\frac{1}{2}$, $-\frac{1}{2}$, $1\frac{1}{2}$, $-\frac{1}{2}$ or $\frac{1}{2}$, $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$, (*b*) for P R = 1 1 $\frac{1}{2}$ $1\frac{1}{2}$ either P′ R′ = $\frac{1}{2}$ $\frac{1}{2}$ 0, 1 or 1, 0, $\frac{1}{2}$ $\frac{1}{2}$ or $1\frac{1}{2}$, $-\frac{1}{2}$, 1 0 or 0, 1, $-\frac{1}{2}$ $1\frac{1}{2}$ and (*c*) for P R = 1, 1, $1\frac{1}{2}$, $\frac{1}{2}$, P′R′ = either $-\frac{1}{2}$, $1\frac{1}{2}$, 0, 1 or 1, 0, $1\frac{1}{2}$ $-\frac{1}{2}$ or $\frac{1}{2}$ $\frac{1}{2}$ 1 0 or 0, 1, $\frac{1}{2}$, $\frac{1}{2}$ The lines which constitute the red E fragment make the RP intersection (at $m = \frac{1}{2}$) and the R′P′ intersection (at $m = 0$) occur at practically the same wave number If we could be certain of this, a large number of these alternatives would disappear and we should be left only with either (1) for P, R $E_1 = E_2 = +1$, $e_1 = +\frac{1}{2}$, $e_2 = +1\frac{1}{2}$ and for P′, R′ $E_1 = E_2 = +\frac{1}{2}$ $e_1 = 0$, $e_2 = +1$ or (2) for P, R $E_1 = E_2 = e_1 = e_2 = +1$ and for P′, R′ $E_1 = E_2 = e_1 = e_2 = +\frac{1}{2}$, or (3) for P, R $E_1 = E_2 = +1$, $e_1 = +1\frac{1}{2}$, $e_2 = +\frac{1}{2}$, and for P′ R $E_1 = E_2 = +\frac{1}{2}$, $e_1 = +1$, $e_2 = 0$

The uncertainty here arises from the fact that the E P and R branches each consist of only two lines, and if any one of these were not the band line there might be a considerable displacement of the R P intersection On the other hand, the conclusion reached is rendered probable from the fact that the spread between the intersections of R P and of R′ P′ steadily diminishes as we pass from the A to the E bands On the evidence at present available I do not see how to distinguish between the alternatives (1) (2) and (3) and these have for the differences of $\{R(m) - P(m+1)\}$ the alternative values either (1) $2b$ or

(2) $4b$ or (3) $6b \simeq 164$ This leaves the moment of inertia of the emitters uncertain by the factors 1, 2 or 3

Another question which must be left open for the present, is the reality or otherwise of the apparent change in the quantum character of the constants $E_1\, E_2\, e_1\, e_2$ in passing from the A to the E bands The view that these quantities are different for the A as compared with the E bands meets with difficulties both in the structure of the bands themselves and also in requiring a change of a continuous character in the values of E etc, in passing from each band to the next An alternative interpretation which is feasible is to give to E, etc, the same values that they have in the E bands in every case, and to put all the variations in the corresponding terms from band to band in the quantities B and in effects arising from the vibrational and possibly also the electronic terms

It is expected that more light will be thrown on these open questions when the alternative red P′ branches and the various fragments which have been found in the green and the blue have been studied more fully

Each of the alternative schemes (1) (2) and (3) requires the lines P (1) and P (1) ($m = 1 \rightarrow m = 2$) to exist, and it appears that in the red lines do occur where these are to be expected, viz —

Table XXIV

Properties									Wave Number	Int	Vertical 1st Diff	Vertical 2nd Diff	Horizontal 1st Diff	Horizontal 2nd Diff
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)						
AP (1) = 6041 01	+		+					2	16548 95	(4)	72 81	14 81	255 12	
BP (1) = 6139 36			++					1	16283 83	(2)	79 87	14 21	256 16	8 96
CP (1) = 6237 49								abs	16027 67	(0)	86 43	14 06	251 71	4 45
*DP (1) = 6337 01							E R(3)	abs	15775 96	(0)	87 11	9 72	246 99	4 72
EP (1) = 6437 81			+					abs?	15528 97	(3)	82 62	9 90		
AP′(1) = 6012 33								2	16627 92	(0)	78 97	11 97	289 89	
BP′(1) = 6119 03			++	0			IV of R(2)	abs	16338 03	(3)	90 73	8 17		
CP′(1) does not exist so far as is known														
DP′(1) = *6340 57		+	−				S_1 (4)	2	15767 10	(6)	87 89	11 77	282 17	
EP (1) = 6456 11							DP (4)	0	15484 93	(0)	75 54	11 54		

* This line is double under high resolution

The vertical differences given in Table XXIV are the vertical differences of the P and P′ branches which would result if these members were put into Tables IV and VII, and the vertical differences given in Table XXVI below are of the same nature The lines BP (1) and CP (1) can be extrapolated accurately from the other P (*m*) lines, and the other lines in Table XXIV lie on the expected position as nearly as it is possible to ascertain it. The strength of AP (1) and AP′ (1) in the first type and at − 252° C is strong evidence in favour of putting these lines into the P and P′ branches The P branches in the green and blue are too feeble to build anything on in this connection.

§ 8 *The Q and Q′ Branches*

I have not, so far, been able to find any combinations between these branches and any of the others, but as the P and R branches alone have been found, as yet, in the green and the blue, all that this implies is that the Q and Q′ and P and R branches have no common initial states As the preceding analysis seems to require with some certainty that $E_1 = E_2 = +1$, at any rate at the E end of the bands, this excludes the value + 1 for E_1 and E_2 for the Q and Q′ branches and leaves as reasonable alternatives $E_1 = e_1 = -1$, 0 or $\pm \frac{1}{2}$ The structure of the bands is able to distinguish between these alternatives If $E_1 = e_1 = 0$ the ratio of the first three first differences of the lines of the branch is approximately as 3 5 7, if $E_1 = e_1 = -1$ it is as 5 7 9, if $E_1 = e_1 = +\frac{1}{2}$ it is as 2 4 6 and if $E_1 = e_2 = -\frac{1}{2}$ it is as 4 6 8 These differences for AQ (*m*) and AQ′ (*m*) are shown alongside each other in Table XXV It will be seen that for Q′ (*m*) the successive first differences are very closely as 2 4 6 and for Q (*m*) as 4 6 8, from which it appears that for Q (*m*) $e = -\frac{1}{2}$ and for Q′ (*m*) $e = +\frac{1}{2}$. Thus the Q′ (*m*) branches appear to have an extra line at the beginning as compared with the Q (*m*) branches

Table XXV —Vertical Differences of AQ (*m*) and AQ′ (*m*)

m.	AQ (m)	1st Diff	2nd Diff	A′Q (m)	1st Diff	2nd Diff
1	16611 43			16692 04		
		15 02			7 52	
2	1659 41		7 25	16684 52		9 44
		22 27			16 96	
3	16574 14		7 55	16667 56		7 71
		29 82			24 67	
4	16544 32		6 77	16642 89		
		36 59				
5	16507 73					

There is however evidence that the line Q (0) forbidden by the adopted selection principle ($m \rightarrow m$ $m \neq 0$) exists in a weak form viz —

Table XXVI

Properties	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Wave Number Int.	Vertical 1st Diff	Vertical 2nd Diff	Horizontal 1st Diff	Horizontal 2nd Diff
AQ (0) = 6014 87								abs	16620 88(0)	9 45	5 57	282 85	
BQ (0) = 6119 00			+ +	0			IV a6 R(3) 153 R(4)	abs	16338 03(3)	7 87	(7 13)	269 77	13 08
CQ (0) = 6221 73	+						IV a6 E(1)	abs	16068 26(4)	7 95	6 02	259 26	10 61
DQ (0) = 6323 77								abs	15809 00(1)	8 27	5 16		
EQ (0) does not exist so far as is known												481 69	
FQ (0) = 6522 50								abs	15327 31(0)	11 38	0 98		

The strength except in the cases of AP (1) and BP (1) and the numerical irregularities, in Tables XXIV and XXVI are probably due to blends the expected positions being occupied by stronger lines claimed by other systems The fact that the weak line 6014 87 (0) does not occur on the first type plate but can be found on McLennan s low pressure plate taken at −252° C from which many ordinarily very strong lines are absent seems to be direct evidence that this line at any rate, is correctly attributed to AQ (0) The Q (0) lines are obviously extremely weak compared with the members of the Q branches which follow them and which constitute the strongest lines in this spectrum under low pressure or first type conditions The difference (7 13) in Table XXVI is got by using the corrected wave number 16316 16 for the blend 6127 40 = BQ (2) [S_2 (2)]

There are five important original Fulcher lines in the red which fail to appear both in the first type discharge and on McLennan s low temperature plates They are AQ (2) — 5991 92 (2) = S_3 BQ (1) = 6093 83 (2) = S_6 CQ (1) = 6197 05 (5) = S_6 DQ (2) = 6302 27 (2) = S_5 and CR (1)* = 6201 15 (5) = S_4 The line 5385 50 (3) assigned to green BR (2) appears to show a like behaviour These facts may be of importance in the further elucidation of the spectrum The intensity of 4683 79 (5) = blue DQ (2) is also anomalous

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* The inclusion of 6201 15 (5) = CR (1) here is perhaps doubtful as owing to the closeness of several strong lines the matter is a little difficult to interpret with the resolution which is applicable.

§ 9 *The Emitters of these Bands.*

It seems most probable that the emitter of Fulcher's bands and the associated bands discussed in this paper is neutral H_2. These bands are the dominant feature of the spectrum of the first type discharge at least in the region between H_α and about λ 5300. The first type discharge cannot be maintained in a normal way below the ionization potential at which the hydrogen molecule is split into the positively charged hydrogen molecule $H_2 +$ and an electron.* In this discharge, when excited at the lower voltages, the luminosity is confined to the neighbourhood of the anode, but the Fulcher lines extend further toward the cathode than the stronger Balmer line H_α. These facts, coupled with the absence of the high quantum number Balmer lines in this spectrum, make it almost certain that the emitters of the Balmer lines are mainly H atoms which have been excited without ionization, and those of the Fulcher lines bodies which either are or have been $H_2 +$.* These considerations do not distinguish between the positively charged hydrogen molecule (excited $H_2 +$) and the neutral hydrogen molecule (excited H_2) formed by the recombination of the $H_2 +$ with an electron, as the possible emitters, but a consideration of the distribution of luminosity and of the mechanism of the discharge, though not decisive, seems to favour the latter alternative.

An important feature of these electron discharges, first observed by Prof. Bazzoni and myself,† is that the first type discharge when first excited with the minimum voltage necessary to do so, starts as a glow covering the anode. As the potential is raised, the glow moves forward and breaks away from the anode, until when the second type discharge strikes, the main glow is lodged on the cathode. Why does the luminosity in the first type discharge show this very definite displacement and also have a fairly sharp boundary? I believe that the reason for this is that recombination between an ion and an electron is far more likely to take place if the relative kinetic energy of the two is comparatively small. The part of the discharge tube at which there are a large number both of slowly moving $H_2 +$ ions and of slowly moving electrons is the region between the equipotential surface, which is distant from the cathode by an amount equal (in volts) to the ionizing voltage, and a similar surface some millimeters nearer the anode. In the first type discharge the luminosity does appear to have a geometrical restriction of just this kind.

The fact that Fulcher's bands are pre-eminently bands which are enhanced by high *electron* current densities, strongly favours excited H_2 as their emitters as against excited H_2+ The spectrum of excited H_2+ should be depressed by high electron densities We should expect it to be enhanced by any process involving the reaction $\enclose{circle}{\mathrm{H}+} + \mathrm{H} \longrightarrow \mathrm{H}_2+$. The first type discharge is probably the least favourable of any kind of hydrogen discharge to this reaction, but it is the one in which Fulcher's bands are most outstanding

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* *Cf.* Richardson and Tanaka, 'Roy. Soc. Proc.,' A, vol. 27, p. 490 (1924).

† Richardson and Bazzoni, 'Phil. Mag.,' vol. 32, p. 433 (1916).

§ 10 *Other Systems*

In addition to the bands apparently connected with Fulcher's and mentioned on p 739 I have found some lines, of which the strongest are 5938 60 ($\nu = 16834$ 34), 5982 54 ($\nu = 16710$ 70) and 6031 80 ($\nu = 16574$ 14), which stand out in Kiuti's* plate and which can be arranged as a P Branch with the same second difference as his Q branch There are also some weaker lines which may belong to them, and others which may be the corresponding R branch. There is, however, a possible alternative way of arranging these lines, and it does not seem possible to settle between the relative merits of the two alternatives without better experimental evidence than exists at present Somewhat similar considerations apply to some lines which appear to be connected with those recently arranged by Curtis.† All these and various other points are being attacked experimentally, but it will probably be some time before information of the definiteness required is forthcoming

In conclusion I should like to thank Mr D B Deodhur for assisting in the examination of the first type discharge, Mr Wilfred Hall for taking several plates with his 21-foot grating, Professor McLennan for allowing me to examine his low temperature plates, and Professor Merton for the helium plate referred to on p 720

§ 11 *Summary.*

A more detailed examination of the spectrum of the first type discharge has shown that there are a number of other lines which belong to the same system as Fulcher's bands. It is proposed to rearrange these lines so that S_2 to S_{-1} form a Q branch, S_4 the first line of an associated R branch to which there is a corresponding P Branch, S_6 and S_5 the first two lines of an associated Q^1 branch, and S_7 the first line of an associated R^1 branch to which there is a corresponding

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* Kiuti, 'Proc Phys. Math Soc of Japan,' vol 5, p. 9 (1923), also Nagaoka Anniversary Volume, p. 193, Tokyo (1925).

† 'Phil Mag.,' vol 1, p 695 (1926)

P^1 branch. This holds throughout the first 5 of the 6 red bands Four similar bands occur in the green and five in the blue, but the branches in those regions which would correspond to the dashed letters have not yet been located with certainty. There is a combination such that R (m) − P $(m + 1)$ has the same value for corresponding lines of corresponding bands in the red, the green and the blue. The quantum structure of the bands is not fully determined, but it is shown that they can be represented by terms of integral and semi-integral type. Reasons are given for believing that the emitter of this band system is the neutral hydrogen molecule H_2 formed and excited by the combination of the ionized hydrogen molecule $H_2 +$ with an electron

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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John Perry

JOHN PERRY—1850–1920

JOHN PERRY was born in Ulster on February 14 1850 the second son of Samuel Perry of Garvagh He attended classes at the Model School Belfast and from 1864 to 1868 served his apprenticeship to the firm of Victor and David Coates of the Lagan Foundry Belfast going through the drawing office and pattern shops In 1868–70 he attended the engineering classes of Prof James Thomson at the Queen s College Belfast being allowed as a special privilege to go through the blacksmith s fitting and erecting shops at the Lagan Foundry during the summer months He attached great importance in later life to the fact that his theoretical and practical instruction thus went on hand in hand He was allowed to graduate early as Bachelor of Engineering in 1870 obtaining first honours and the Gold Medal and in the same year obtained a Whitworth Scholarship and accepted a post as second mathematical master and lecturer in physics at Clifton College where he established a physical laboratory and a workshop in 1871 It has often been stated that these were the first established at any school but Perry found later that there had been a workshop previously at Rossall and in making the acknowledgment he added These ideas were not mine they were those of the headmaster [Dr Percival]

He left Clifton in 1874 to become the Honorary Assistant of Prof Sir William Thomson at Glasgow and in 1875 accepted a Joint Professorship of Engineering at the Imperial College of Engineering in Tokio Japan He was on duty from September 9 1875 to September 8 1878 and gave lectures on steam structure and hydrodynamics In all some 200 students attended his lectures some of whom became professors in the Engineering College in succession to him some again his pupils in London and some important personages in industrial circles Prof Perry and his contemporaries may be said to have founded the development of Japanese industry Special mention should be made of the fact that the professors occupied themselves ardently in researches beside their teaching duties (*Letter from Prof Shin Hirayama March 26 1926*)

This last sentence has a special reference to the association of John Perry with W E Ayrton *in a series of* brilliant researches The partnership was one of great advantage to both men and was so congenial that for a time they shared equally all their receipts even the lecture fees that either of them might earn It continued after their return to England up to the year 1891 when their last joint paper (of 56) was published

Perry returned to England in 1879 organized the works of Messrs Latimer Clark Muirhead & Co became Examiner in Engineering to the City and Guilds of London Institute, and in 1882 was appointed Professor of Mechanical Engineering at the City and Guilds of London Technical College in Finsbury Ayrton had left Japan in 1878, and had prepared the way for this College by starting (with H E Armstrong as his only colleague) technical instruction to a class of one old man and a boy of 14 But progress was very rapid, especially when Perry joined the other two He remained 15 years at the College, and while there wrote his *Practical Mechanics*, 1883, and his *Spinning Tops* (1890), the development of a British Association lecture to working men But his appointment at the Royal College of Science in 1896 led to a more copious educational output The *Calculus for Engineers* and *Applied Mechanics* both appeared in 1897, *Steam and Practical Mathematics* in 1899, and *England's Neglect of Science* in 1901, the year in which, at the Glasgow meeting of the British Association, he opened a crusade for the better teaching of mathematics He retired from his professorship at the Royal College of Science in 1913, but in his retirement he was constantly busy with engineering problems, especially that of the gyro-compass, on which he again worked in the happiest circumstances of collaboration, this time with Mr S G Brown, F R S, his nephew by marriage He was also devoted to his work as Treasurer of the British Association, which he took over from Carey Foster in 1904 In 1920 a failure in health led him to take a long voyage to South America with Mr and Mrs S G Brown But he returned without apparent benefit, and took to his bed a week later, when it was found that he must have contracted scurvy on the voyage After a few days' serious illness he died peacefully on August 4 He had married in 1879 Miss Alice Jowitt, of Sheffield, who died childless in 1904, and he was laid beside her in the churchyard at Wendover, where they had a country cottage

In the career of which this is a bare outline, two features stand out clearly—the fertile partnership with Ayrton and the campaign for improved methods of teaching The partnership began almost immediately after Perry reached Japan, for in a printed list of 39 papers prepared about 1880 it is stated that all but four were published in conjunction with Prof Ayrton, and of these, three are dated 1876, ten 1877, eight 1878, seven 1879, while seven are undated The titles indicate varied activity there are two relating to earthquakes, which fascinated most of the young Englishmen who were invited about this time to teach the Japanese Western culture, and which continued to interest Perry to the end of his life, two are on heat conduction in stone, and probably led to Perry's later investigation on the cooling of the earth; there is one on "The Music of Colour and Visible Motion" (*Phil Mag*, 1879), another on "A Dispersion Photometer," yet another on "The Magic Mirror of Japan" (*R.S*, 1878); and there is a joint investigation on stresses in continuous Beams, which formed the basis of some lectures to students, but the great majority are electrical investigations of one kind or another. They begin with studies of the quadrant electrometer, of defective insulators, and of lightning conductors, and these led on to "The Importance of a General System of Simultaneous Observations of Atmospheric Electricity" (*Jour Soc Tel. Eng*, 1877) Two Royal Society papers in the list are on the "Contact Theory of Voltaic Action," on which other papers followed later The *Engineer* for November 25, 1881, contains a report specially requested from the collaborators on "The Efficiency of Electric Lamps" as deduced from exhibits at the Paris Electrical Exhibition, prefaced by the editorial remark :—

> "It deals for the first time with questions that have hitherto been carefully avoided, but which are of great importance"

Ayrton and Perry made the first determinations of the dielectric constant of gases, on which followed an important memoir on the significance of this constant in the definition of the electrostatic unit of quantity They wrote on the viscosity of dielectrics, the theory of terrestrial magnetism, electrolytic polarization, telegraph tests, and they produced the first electric tricycle in 1882 The volume of their early work was so great as to draw from Clerk-Maxwell the jest that "the centre of electrical gravity seemed to have shifted to Japan."

Such a partnership depends for success as much on differences between the components as on what they have in common One little incident may be given in illustration Perry enjoyed holidays, Ayrton did not Perry went for a six weeks' holiday, and Ayrton wrote a letter to him every few days about matters he thought urgent When at last Perry returned to England, Ayrton met him at the station, enquiring eagerly for the results Perry drove him back to his house in Brunswick Square, went into his study, opened his bag and poured out all the letters unopened, with the remark, "Ayrton, I was on holiday, now I will deal with this work"

It is, fortunately, not necessary to discuss the question whether Perry's direct contributions to knowledge, or those which flowed from his own teaching and his influence on other teachers, are the more important Certainly he exerted a profound influence on the mathematical teaching of recent years. The Mathematical Association has just published (1926) a Report on the "Teaching of Mathematics to Evening Technical Students," which opens in the following words :-

> "Mathematics has long been recognised as an important element in the education of engineering and other technical students. Much thought has been devoted to the problem of presenting mathematical ideas in such a form that they can be readily assimilated and applied to technical problems At one time, the presentation was undoubtedly too abstract This tendency has now disappeared, chiefly owing to the efforts of the late Prof Perry. His methods have been adopted very widely When they were first introduced, they aroused great enthusiasm, and it was hoped that henceforth no difficulty would be experienced in imparting a good

> working knowledge of mathematics to every student of average capacity. Subsequent experience has proved that these hopes were too sanguine Some very good work has been done, both by teachers and students, and yet, in the opinion of many, the results obtained are somewhat disappointing."

Doubtless opinion will vary, both in time and place, as to the value of Perry's methods. He himself ardently believed in them and lost no opportunity of pressing them on the attention of others, though his ideas did not reach a wide circle of mathematicians until the discussion meeting at the British Association in 1901 But, as an instance, both of the methods themselves and of the way he pressed them upon the attention of others, we may quote a passage from a statement made by him to a Special Committee of the London School Board on December 14, 1887 —

"On leaving the foundry I became Science Master and Assistant Mathematical Master at Clifton College, Bristol The ages of the boys ranged from 12 to 18 I established there a school workshop and a physics and mechanics laboratory These were the first institutions of their kind established in any school Here students went through a series of quantitative experiments I will describe one of these experiments in connection with mechanics There is a piece of apparatus which is generally employed to illustrate the laws of blocks and tackle by which a man's pulling force can lift a great weight In this apparatus a small weight is shown to be able to balance a much larger weight The student having been told about this in a lecture, he is taken to the laboratory, where he finds printed instructions on the piece of apparatus. A scale pan containing the larger weight is, say A, and that of the smaller is B He puts a certain weight in A. He now adds to B until, on giving B a start downwards, a steady motion of the apparatus results He now says that B balances A and friction He takes another weight A and repeats, and so on until he has obtained a great number of observations He now plots the weights B which balance weights A on squared paper, obtains the law connecting them, obtains the law for efficiency of the machine, and obtains the law connecting friction and load. It is impossible for a boy to perform this process without obtaining exact ideas of work, loss of energy by friction, co-ordinate geometry, the meaning of a physical law, and the algebraic expression of a physical law His hand and eye become educated His mental power is continually exercised, and becomes enormously increased I have observed these facts in many hundreds of students The most curious fact observable is that when students learn in this way, by a proper amalgamation of, say, two lectures, three hours' numerical exercise work, and three hours' laboratory work a week, and especially if they have another three hours at mechanical drawing, not one of a great class of even young boys seems to be lazy or uninterested in his work.

"The above experiment made by the student is somewhat similar to that which a practical engineer may have to make on a steam engine or other large motor, and for which he will get perhaps a fee of fifty guineas. Three or four students at a time work on one piece of apparatus for three hours a week By this means, in a room 30 feet by 20, it is possible during a week to give 200 boys, in batches of twenty, this kind of instruction It is necessary that the piece of apparatus should not be used for any other experiment When the student has experimented with one piece of apparatus, he has to pursue a similar course with something else The cost of the apparatus for these experiments, when calculated per head, is not very great This method of instruction was not very completely carried out at Clifton College My ideas, which are probably due to a book written by Dr Ball, were then unformed, but they have gradually been developing In Japan the system was more fully elaborated and tested, and at the Finsbury College it was complete in 1880 In Japan the ages of my students were from 14 to 20 The only scientific knowledge they possessed on coming under my instruction was a slight acquaintance with mathematics I think that the experience in teaching I got there has been of very great use to me since my return to England The system of teaching engineering was very perfect The students were sent to large works in the summer time, and thus a college education was combined with that of the workshop Many of my students are now managers of large works in Japan

"I consider that the problem of Middle Class Technical Education is completely solved The experiment, which has been carried on at Finsbury during the last eight years, has proved that the theories of Prof Ayrton, Dr Armstrong, and myself were perfectly correct I have been testing these theories all my life"

Perry's general idea was to bridge the gap between engineers and mathematicians He wanted the engineers to think scientifically and the mathematicians to convert their formulæ into concrete facts, especially by the use of squared paper

> "Before 1876 sheets of squared paper were very expensive, they were only used by a few people in important work. In that year Prof Ayrton and I began to use it extensively in Japan, and when we returned to London and introduced at the Finsbury Technical College our methods of teaching mathematics and mechanical and electrical engineering and laboratory work, which have now become so common, we saw that one essential thing was the manufacture of cheap squared paper It can now be bought for 6*d.* a quire instead of 8*d* per sheet Our students treat it almost like scribbling paper . It is of importance that the student should use many sheets of squared paper, use them lavishly" (Perry's *Elementary Practical Mathematics*, chap. IX)

The broadcasting of squared paper, though a detail, is a detail of great importance, and representative of the effects of Perry's campaign The existence of mathematical laboratories at some of our public schools is another symbol, and there are by this time many school textbooks to show Perry's influence, though in some of them there may be no direct indication of it beyond the date of publication

> "To many mathematicians," writes an eminent engineer (Prof. E. G. Coker) recently, "Perry was no doubt illogical, and everything that he should not be as a mathematician, but there is, I think, little doubt that to engineers he was most useful, and his influence on his time was tremendous He was so very stimulating and helpful. He brought home to us what mathematics meant, and could do, and was *not* fitted to do, in a way that was only possible for a man who had been obliged to pick up knowledge as he could while going through an arduous training in engineering workshops" (February 18, 1926.)

Such testimony and results would not be forthcoming had Perry's qualifications been merely intellectual, he had a great capacity for making friends of his students, and, indeed, of all with whom he came into contact On his leaving Japan, 56 students presented him with a photograph of themselves with him in their midst, appending their names to an affectionate farewell address, in which they regret that so many of his pupils are "scattered about in different parts of this country, and are, without doubt, exceedingly sorry for their absence"

Again, after he retired from the College of Science, his old students at South Kensington and Finsbury collected a sufficient sum of money for a John Perry medal, stamped with his portrait, to be awarded annually The honour was very highly appreciated by him. It would scarcely be just to omit all mention of his great and continued generosity to poor students.

He was often called upon for speeches at gatherings of his English students, responding in genial vein, *e g*, "When I am among scientific men I pose as a professional man—and when I am among professional people I pose as a scientific man—and when I find both professional and scientific people together I try to hold my tongue" The last speech he made was on the voyage which had so fatal a sequel Having been asked to present the prizes to the children after their sports, he appeared in a red robe as Father Christmas drawing a Teddy Bear on wheels, and made the children a fascinating speech on the great privileges their parents enjoyed in possessing such wonderful children. This was about five weeks before his death

He was a great reader and declared that to wake in the night was a real pleasure to him, as an additional opportunity for reading He acquired the habit of unbinding books and separating them into separate portions of a few pages, which he could carry in his pocket without inconvenience. His favourites (especially the Bible and Macaulay's Essays) he read over and over again in this way, but he read new novels voraciously, and lent them freely to others, not merely here in England but during his early days in Japan.

He conscientiously tried to acquire a liking for opera, but after some really painful struggles gave it up and returned to his Irish melodies, which he loved. He was a keen debater, and as such took an enthusiastic part in the proceedings of the Kensington Parliament, which held meetings about 1889.

Towards the close of his life he was invited to give some important advice in South Africa. The British Government chose him to represent them on a Committee to decide on the best method of administering the Otto Beit bequest of half-a-million The main point to be decided was centralization, or scattering, whether to have one big college somewhere, or a number spread over the Continent The Committee made extended travels in a railway coach, and ultimately reported in favour of a college of similar importance in each State Perry dissented, and his minority report in favour of a specially important college at Cape Town, with minor colleges elsewhere, was included He felt strongly the desirability of having one college strong enough to attract professors of first-rate importance In the end his suggestions were accepted *in toto*, even down to the details of salaries.

H H. T

[For reasons which need not concern us, it was not until January, 1926, that any request reached me to undertake to write something about my friend John Perry. It was a request which I never thought of refusing if no one better qualified was available; but I was acutely conscious of my ignorance of his work and doings before 1913, when he and I became associated in the service of the British Association, of which he had been Treasurer since 1904. This disability has, however, been remedied, so far as possible, by the kindness of Mrs S. G Brown, Perry's niece, who has allowed me to consult her uncle's books and papers, especially a collection of scraps intended for a scrap book though never bound up —H. H. T]

PERCIVAL SPENCER UMFREVILLE PICKERING—1858–1920

SPENCER PICKERING, who died at the age of 62, on December 5, 1920, after a long illness, was a fine example of the sturdy and independent-minded type of Englishman Free by the accident of birth to choose his own career, he devoted himself to science, and produced work which, although concerned with various widely different branches, was throughout characterised by a disregard of authority and reliance on his own judgment, based on the results of carefully-planned and well-executed experiments

He was born in 1858, and was the son of Percival Andree Pickering, Q C, Recorder of Pontefract, and Anna Maria Wilhelmina Stanhope, granddaughter of Coke, of Norfolk, the celebrated agriculturist, who was created Earl of Leicester in 1837 He felt much pride in his descent, and made elaborate inquiries into the history of the various branches of his ancestry Both his father and mother were representatives of distinguished and ancient families, concerning which his surviving younger sister Wilhelmina (Mrs A. W W Stirling) has written several fascinating volumes He was educated at Eton, and entered Balliol on January 19, 1877, where he remained until the Lent term 1880 He became Brackenbury Natural Science scholar, and took the Final Honours in Natural Science in 1879 Even as a school boy he had been devoted to chemistry, and it was whilst experimenting in the laboratory provided for him by his father at his home in Bryanstone Square that, as the result of an explosion, his eye received the serious injury which ultimately resulted in its removal Before he left Oxford he had published several papers in the Journal of the Chemical Society In the following year he took up the only academic appointment he ever held, becoming Lecturer in Chemistry at Bedford College, a position which he retained until 1887 He continued to work in the private laboratory at Bryanstone Square, first pursuing the subjects which had already attracted his attention at Oxford Gradually he became interested in the problem of the nature of solutions, until the whole of his energy was devoted to the experimental study of this subject After 1896, probably disappointed at the reception accorded to his views by the scientific world, he ceased to work on these lines The almost innumerable determinations of density, freezing point, conductivity, etc., involved in this work were carried out single-handed with a high degree of accuracy, and the results were embodied in a long series of more than 70 papers published between 1887 and 1896, in which, in the face of much criticism, he steadfastly maintained the hydrate theory of solutions From this subject Pickering turned to an entirely different branch of investigation, which he approached with his characteristic disregard for all conventional ideas. How this came about is well told in

P Spencer U Pickering

an article in Nature (19.9.'95) on the establishment of the Woburn Experimental Fruit Farm, which is quoted in the preface of "Science and Fruit Growing" (Macmillan & Co., London, 1919), the book in which the Duke of Bedford and he summed up their joint experience of 25 years. "The object of this institution, which, under the above somewhat unpretentious title, has been established by the joint action of the Duke of Bedford and Mr Spencer Pickering, F.R S, in order to supply what has hitherto been a great national want, is to provide an experimental station where all matters connected with horticulture, and especially with the culture of hardy fruits, may be investigated both from the scientific and practical point of view

"The origin of such an enterprise is always a matter of some interest, and it becomes all the more so in after years, when, too often, the details of its conception and evolution are irretrievably lost. In the present instance, we may trace the origin to an accident in a chemical laboratory It was owing to such an accident some years ago that Mr Pickering, whose work in physical chemistry is well known, was driven to seek health in a partial existence in the country Not having the means, however, to procure this in the orthodox manner without abandoning his scientific work, he resorted to the somewhat unusual means of getting air and exercise by becoming an agricultural labourer at Rothamsted From an agricultural labourer to a small farmer and landowner the steps were not so tedious as is generally the case, and for some years past Mr Pickering has turned his attention, after the manner of many landowners, to horticulture and practical fructiculture To anyone of a scientific turn of mind the unsatisfactory basis on which the culture of fruit depends cannot fail to be apparent Its present condition is little better than that of agriculture some fifty years ago. It rests mainly on the hard-earned and often one-sided experience of practical men, gardeners for the most part, or nurserymen.

"But the pressure of business will rarely allow a nurseryman to indulge in anything approaching to systematic research, and even when he does obtain any important results they are liable to be looked on askance, as being possibly tinctured by mercenary considerations Moreover, even amongst the highest practical authorities there is hardly a single point in the cultivation of fruit on which unanimity of opinion prevails, indeed, on some of even the most elementary processes there seem to be as many opinions as there are so-called authorities

"The desirability of having some station where such matters might be patiently investigated, and from which results might issue free from any taint of commercial expediency, was evident to Mr Pickering, and not having himself the capital or land necessary for such an undertaking, he applied for assistance to a former college friend, the Duke of Bedford The Dukes of Bedford have during generations past identified themselves with the progress of agriculture and horticulture the present holder of the title showing no tendency to be eclipsed by his predecessors in these matters As was probable such a scheme met with the hearty approval of the Duke and the result was the establishment of the present institution conducted jointly by himself and Mr Pickering

The fruit farm is on the Duke s land near Ridgmont station and almost adjoins the land which is given up to the use of the Royal Agricultural Society as an experimental agricultural station About twenty acres have been devoted to the purpose and of this some fifteen have already been planted

At the experimental farm all aspects of fruit growing were carefully investigated nothing being taken for granted—and the results were published in a series of reports the 17th of which appeared in 1920 and were summarised in the work quoted above

The fruit farm was admirably planned and the results of the experiments were in many cases obvious and striking to the eye The writer well remembers the convincing picture presented by the experimental plots some ten years after their establishment and there is no doubt that this ocular demonstration was of great value in spreading among fruit growers the new and often startling information derived from the experiments His association with Harpenden was strengthened by the purchase of a house in 1885 which became his permanent home in 1902 in which year he gave up his London house Here he found congenial society in the presence of Gilbert Lawes Warrington and Lyddeker and in later years of Hall and Russell He was a member of the Athenæum and in 1890 was elected a Fellow of the Royal Society He married in 1897 Ethel Wilmot whom he had thanked in his 1890 paper on Solution as a little girl who had devoted all her spare time to the laborious calculations involved in the present work They became inseparable companions in the home and in the walks to which at one time he was devoted Though austere in manner Pickering was endowed with a strong infusion of that artistic and romantic temperament which showed itself so markedly in his sisters one of whom Evelyn a distinguished artist married William de Morgan whilst the second Wilhelmina (Mrs Stirling) is a well known authoress to whose works allusion has already been made This revealed itself throughout his life in his love of music and his taste in art and literature and found final expression in the romantic instructions for his burial on the Devon coast He left no children and placed his private fortune subject to his widow s life interest in the hands of the Royal Society for the promotion of research in science

His views on solution are to be found fully expounded in an article in the Muir Morley revision of Watt s Dictionary of Chemistry (vol 4 pp 492–6) following one by Arrhenius in which the views of the Van t Hoff school of physical chemistry were expressed His contention that hydrates exist in solution is now generally accepted whereas his deduction of the composition of these hydrates from discontinuities in the first or even second differentials of his curves of densities etc which led him to believe in the evidence of highly complex hydrates such as H_2SO_4 5 000 H_2O has never been generally admitted as convincing

Pickering was not only firmly convinced of the existence and preponderating importance of hydrates in solution but was also strongly opposed to Arrhenius theory of electrolytic dissociation seeking to explain the phenomena on which this theory was based on grounds of residual affinity and increased freedom of motion of the atoms in the molecule

In the event his views were overwhelmed by the rising flood of physical chemistry and it was only after a considerable interval that hydration of molecules and ions in aqueous solutions became generally recognized

Among the many and important results arising from the work at the experimental fruit farm two or three may be selected as being typical of his methods as well as of intrinsic interest The first concerns the method of planting fruit trees and was at first received with incredulity and the most hostile criticism The orthodox method of planting was to spread the roots well out trimming them when necessary carefully with a knife and then replacing the soil and making it firm avoiding as far as possible any injury to the root The results of the Woburn experiments led to a procedure which was the exact antithesis of this It was found that even when the roots were huddled into a small hole and the soil rammed tightly round them by the aid of a rammer regardless of mechanical injury in the great majority of cases the trees grew better usually even in the first year after planting—more certainly in the second year Nearly 1 500 trees were used in these experiments which were extended to a variety of soils and situations throughout the country So opposed to general practice were the conditions that it was difficult to ensure the proper carrying out of the experiments by independent observers trained in the orthodox methods but the results clearly showed that except in very light soils and in the London clay planting the tree in *gatepost fashion* undoubtedly benefited it

Of considerable interest are the observations and experiments on the effect of grass on the growth of fruit trees which were extended to the more general problem of the toxic effect of one crop on another This work arose from the observation that the growth of the trees of certain of the experimental plots which had been grassed over was seriously affected This difficult question was investigated in the most careful manner the various possible factors such as changes in nourishment aeration and water supply temperature the physical and chemical conditions of the soil etc, being separately examined often by extremely ingenious methods The final result was to establish beyond all reasonable doubt that the deleterious effect which is exerted by a large number of plants on others growing in association with them is due to a toxic substance, probably excreted by the roots There is still some mystery as to the nature of the toxin for it cannot be detected in the soil in which the grass is grown or in the washings from soil in which grass is growing

Another subject to which a considerable amount of attention was paid at Woburn was the composition and proper use of insecticides and fungicides This led Pickering back to the subject of basic salts, which had occupied him in his early days, and he published from 1907–1917 a long series of papers on the basic salts of copper, in which a large number of such compounds, which are present in the mixtures used for spraying plants, were described and an attempt made to represent their constitution by chemical formulæ The study of insecticides also led to work on emulsification, and he succeeded in obtaining remarkable semi-solid true emulsions, containing as much as 99 per cent. of paraffin oil dispersed in only 1 per cent of a 1 per cent. solution of soap He also found that insoluble precipitates, such as the basic sulphates of iron and copper, could replace the soap usually employed as emulsifier, yielding extremely stable emulsions, admirably adapted for use as insecticides or fungicides

The work at Woburn is generally regarded, in the words of Sir Daniel Hall, "as the most substantial contribution of the last hundred years to the study of fruit tree development" Its importance resides not only in the value of the actual results obtained, striking as these are, but in the example afforded of the strict application of scientific principles to the investigation of horticultural problems.

A. H

[The writer is indebted to Sir Edward Russell for permission to utilise the information contained in the Obituary Notices written by him for the Chemical and Biochemical Societies.]

James Dewey

SIR JAMES DEWAR 1842—1923

James Dewar was born September 20 1842 at Kincardine-on Forth the youngest of seven sons His father a vintner kept the chief inn and was said by his son to have been a man of marked originality of character—a Presbyterian of the section known as the Auld Lichts The son was true to breed—ever the Presbyter!

As a lad he was fond of music and played the flute fairly well before he was ten years old About this time he met with an accident falling through the ice this was followed by an attack of rheumatic fever and he was an invalid obliged to go about on crutches during a couple of years His lungs were weakened and he had to give up the flute the village counted a fiddler and it is said the father called the fiddler in to cheer the delicate boy Fiddles were then common in Scotland as there was much coastal trade with Italy in those days I had it from Dewar himself that during this period he was brought much into contact with the village joiner and practised his hand in making fiddles this training in manual dexterity he often said was the foundation of his manipulative skill indeed he regarded it as the determining event in his career He would dwell particularly upon the importance of some real task being undertaken in such work and always deprecated mere disciplinary routine exercises He is said to have made a number of fiddles the one he retained is labelled James Dewar 1854 so was made when he was twelve years old It was a good instrument and was played upon with effect at his golden wedding

When recovered from his accident he went to the Dollar Academy then and long a famous school He took the first prize for Mathematics a gold medal also the first prize in Natural Philosophy in his last year Leaving school he went to Edinburgh University carrying with him the fiddle made five years before with his own hands as his recommendation He entered as an Arts student in 1859 and lived with his brother Alexander who was then nearly through his medical course They lodged with two elderly ladies under whose roof James Dewar remained up to the time of his marriage August 8 1871 The books in his library show that he took prizes in Prof Kelland s second mathematical class in 1860 and in his third mathematics class in 1861 In 1861 he took the prize in the Second Division of Natural Philosophy and a prize for eminent success in Natural Philosophy in Prof Tait s class In 1862 he again took two prizes in the First Division of the Natural Philosophy class

He worked in the laboratory of James David Forbes the distinguished Professor of Natural Philosophy in the University who discovered the polarization of heat and was noted as a glacial geologist and in many other ways a man to whom Ruskin was deeply attached When Forbes left to become Principal at St Andrew s Dewar became the first demonstrator to Lyon Playfair the Professor of Chemistry We can picture him rendering no little service to Playfair, during the years he was his assistant through his dexterity and resourcefulness probably he taught Playfair not a little , the teacher in those days was a pioneer not a mere lecturing machine In this way he was brought into direct contact with two of the most powerful intellects of the day—two men whose characteristic was not only absolute honesty and intensity of purpose but an altogether unusual breadth of outlook Before going to Edinburgh in 1858 Playfair had taught in London in the Royal School of Mines but had also been associated with Liebig in his triumphal progress throughout England as an agricultural propagandist also with Prince Albert over the 1851 Exhibition He had already fully served his apprenticeship as a statesman

On Playfair s retirement in 1868 Dewar became assistant under his successor, Crum Brown and was with him until 1873 or 1874 he taught the Medical laboratory class whilst J Y Buchanan had charge of the ordinary class Again he was in contact with a remarkable man—a man of astounding versatility who would have been a great chemist had he confined himself to chemistry

In 1869 he was appointed Lecturer and later Professor in the Royal Veterinary College In 1873 he also became assistant chemist to the Highland and Agricultural Society of Scotland and delivered district lectures for this body

In 1875 he was appointed Jacksonian Professor of Natural Experimental Philosophy in the University of Cambridge He never carried out the prime duty of his office—the discovery of a cure for the gout—though in early days he sought unsuccessfully for the qualification which might have helped in the work unfortunately he only spoilt his digestion and so in later years was perforce an extraordinarily careful liver

In Cambridge he found no tradition of practical achievement to influence him His colleague Liveing and the Master of his College Dr Porter were perhaps the only men who fathomed his outstanding ability The crudity of youth was still upon him and the free manners of a Scottish University were not those of conventional Cambridge—his sometimes imprecatory style was not thought quite *comme il faut* by the good No attempt was made to tame him or provide means for the development of his special gift of manipulative skill Yet he soon began to exercise an influence which probably has had more to do with the marvellous recent advance of the Chemical School at Cambridge than is commonly supposed The fine volume of collected researches in spectroscopy which Prof Liveing and he published a few years ago is a memorial not merely to their activity but of the example they set as exact observers in a field which at that time was in sore need of cautious workers

Two years after his appointment at Cambridge he also became Fullerian Professor of Chemistry at the Royal Institution London He had twice lectured there previously on the work he had done with McKendrick The second lecture (March 31 1876) his trial trip was probably the most carefully prepared certainly the most logical discourse he ever delivered I well recollect how fascinated some of us were by it

Even if it be possible for a man to serve two masters the task becomes beyond human power when ghosts aid one of them As an artist Dewar had the innate belief of primitive man in ghosts and in the Royal Institution laboratory miserable as was the accommodation it afforded the ghosts of Davy and Faraday were ever about him To have served the Institution honourably in a way to justify mention in history on a par with them is an achievement he in his modesty scarce contemplated as possible and yet he ever aimed at it The feeling that he had so much exceeded Faraday s period of office and not only maintained but also steadily improved the quality of his work, I have reason to think was year by year a more and more powerful mainspring of action in the indomitable fight against circumstances which he waged during these late bitter times of strife He was a terrible pessimist

Dewar was not great as a teacher His mind was of too original and impatient a type He never suffered fools gladly and students are too apt to be foolish at our old Universities even to ape the part of superior beings His forte lay in directing competent hands not in forming them He worked himself and through skilled assistants not through pupils He was violently impatient of failure in manipulation and his work was almost entirely manipulatory He therefore never created a school The pity of it is that circumstances were such that he never had a properly large staff That he accomplished so much with the assistance of the few able men who have aided him is proof of his exceptional skill as a director It is unfortunate that the Davy Faraday laboratory was not from the beginning organised on lines which would have placed its resources in his hands rather than at the disposal of undirected individual workers it is a grievous fact that he leaves no followers trained to use his incomparable methods

Nominally a chemist Dewar s work lay in fields of his own creation not borderlands but regions before uncultivated He was no mere experimentalist but an artist to his finger tips music came next to science in his affections

Though deeply read and a great lover of poetry and literature he lacked the gift of ready literary expression -except in his letters and conversation—and was often an incoherent lecturer yet his lectures were the most masterly and fascinating displays ever witnessed He set a standard which has made the Royal Institution table remarkable throughout the world Faraday was celebrated for the simplicity of his style—Dewar is to be thought of on account of the daring of his displays, the wonderful refinement and appositeness of his demonstrations, all most carefully arranged and rehearsed in advance He was a great scientific actor playing plays with the most thrilling of plots and entirely original special scenery for each performance His manner, his ' brogue " even his impatience gave a peculiar charm to the impression he produced , but you did well to have been behind the scenes if you wished to gather the full meaning of his message His demonstrations were unique in character , few realise the infinite loving care he devoted to their preparation In their simplicity they were often profound I can never forget the impression I received when I first saw him burn diamond under liquid air—the gradual accretion of the carbon dioxide snow shower and the blueing of the fluid by ozone, also demonstrated by the iodine test , then the rapid uprush of the mercury in a barometer tube full of air when the tube was cooled with liquid hydrogen , it all but knocked the top off or again the production of ozone at the surface of solid oxygen by the impact of ultra violet radiations At such moments—and there were many such—the heart beat with joy at the significance of his feats of inspiration

He began to publish in 1867 His first paper, read to the Royal Society of Edinburgh on February 4th, was on the Oxidation of Phenyl Alcohol In it was described a sort of lazy-tongs method of representing carbon compounds , seven different ways of representing benzene were shown Through this he was brought under Kekulé s notice with whom he spent the summer of 1867 in Ghent He was thus brought into contact with the master mind in theoretical chemistry of that time and with his assistant Korner, a laboratory worker of supreme ability

During the period 1867-75 he did a great amount of work on a variety of subjects—chemical biological and physical he then laid the foundation of nearly all his later discoveries He was associated with Dittmar, with Gamgee, with McKendrick and with Tait Possibly, indeed probably, these men all worked with him at his suggestion McKendrick tells the story, in a private Autobiography, how one day, at the Veterinary College, a young man introduced himself to him and said ' You and I should know each other, Dr McKendrick He knew him to be James Dewar and had seen his name frequently on the Royal Society of Edinburgh programme A few days later they met in the quadrangle of the University and Dewar suggested the research on the effect of light on the eye

The influences to which he was exposed, while an apprentice and subsequently in Edinburgh, were such that, given innate ability, it is not difficult to understand his scientific upgrowth , his development on the artistic side, the rapidity with which the rough places were made smooth, cannot well be explained

—apparently he just grew to his environment but largely it seems, to one he himself created

He was probably in full touch with medicine through his brother Dr Alexander Dewar assistant to Prof Syme It is clear that before coming South he had been in close contact with a large circle of remarkable men who fascinated both by his scientific ability and his superlative social qualities had taken him to their hearts

It cannot be said that Dewar came to Cambridge to conquer He made no particular mark there essentially a man of action not built on lines of mere scholarship his great gifts were unperceived The conditions were primitive as compared with those of to-day far less inspiring than in the northern capital In Edinburgh he had been among men who were all alert and he had led a Bohemian life in Cambridge he was confronted by a dour respectability and the damns with which he praised were sometimes far from faint Few of the dons could appreciate his genius the importance of experimental science was not then recognised At no time was the attempt made to capture him and build him a special nest even when his fame was being spread abroad in connection with inquiry at low temperatures Still he had Clerk Maxwell and Stokes as scientific friends—men who could appreciate him Soon he made another and in so doing gained what must be regarded as the greatest and most significant victory of his life I may be permitted to use a phrase current among us in those early days—it so exactly describes the situation he made the Liveing speak In fact he was almost immediately adopted by his senior colleague Prof Liveing whom he induced to sit down at the spectroscope with him not only at Cambridge but sometimes also in London where the work was also carried on because of the more powerful instrumental appliances at hand The association speaks volumes for both men it was the completion of Dewar's education The nobility of Liveing's character was recognised everywhere, there can never have been much to object to in a man with whom one so stern in his moral outlook yet gentle withal could rapidly ally himself and take to his heart Smaller minds could not see so far and at times there were disagreements let it be said openly he was never popular he never suffered fools gladly and he let this be known He was unlucky too in the choice of an assistant who proved disloyal Factions arose So the University lost a great opportunity but the Royal Institution gained the entire devotion of a master mind who built himself into its fabric in a way which even Faraday never accomplished Few can realise with what fervour he served its interests—what his devotion meant—the depth of moral purpose in the man in his character He rendered service not only by his scientific conquests in the laboratory but to an extent which cannot be defined also on the social side his wife greatly aiding him He rapidly made himself a power in the outside world and attracted all sorts and conditions of men making them not merely servants but willing slaves of the Institution The men who aided him are mostly gone To reconstruct the social fabric on the broad basis upon which he built will not be easy

Why did he succeed there, not at Cambridge ?

No artist can brook University conditions and restraints we seem not to realise how entirely we are taking the life—the morality, too—out of science by our competitive system particularly by placing the work of inquiry under Civil Service conditions and making it an onus upon the examinee a service rather than a work of love if not a reverent sacrifice

He came to the Royal Institution a Bohemian and found himself free from control and professorial red tape obligations, in a Bohemian atmosphere—for surely Rumford was a Bohemian and so was Davy, even Faraday was in his quiet way Let it only be whispered—Dewar once told me that he had it from De la Rue that when a young man, he had ventured to visit the 'Poses Plastiques and, to his surprise, saw Faraday sitting in a front seat Dewar had nought of the pedagogue in him, though much of the Presbyter—it irked him to lecture to regular schedule When, however, his subject possessed him those who heard and understood him perforce said —

I met a seer,
Passing the hues and objects of the world,
The fields of art and learning, pleasure, sense,
To glean eidôlons

The theatre of the Royal Institution has been the resort of artists for generations and here he found an appreciative audience Here also he found a studio to his liking full of the ghosts of sciential heroes, he was free to visit it at all hours of the day and night Being an incarnate experimenter, he gradually found full opportunity to exercise his bent and his imagination to exercise the fingers so well developed on his fiddles in his youth Not only was the constructive lust in him, but burnt into his soul was the sense of accuracy and artistic finish

The art of discovery, as a systematic pursuit, is only gradually learnt and choice of subject is not easy—it comes more from the suggestion of opportunity than from inspiration Faraday only came to his climax when he was forty years old The value of experience in scientific work is not sufficiently recognised Dewar began his work in the South in a rather arid period, still an undercurrent was gathering strength and was soon to burst into flood He passed through a period of heat before settling down to the mature respectability of a cold more than arctic

Dewar was ever a hero worshipper—but he was select in his choice The one for whom he had greatest reverence, in his early days, was the French chemist St Claire Deville, a classic figure in the history of our science It was he who introduced the term "disassociation" or "dissociation" to express the condition of reversible interaction, especially at high temperatures, common to all chemical change (that of radio-active material excepted) Dewar was fascinated by the beauty of Deville's experimental methods and the precision of his treatment of the problem Hence it was probably, that he, with Liveing, entered the arena against Lockyer, whose speculations on the dissociation of the elements at high temperatures were then beginning to fill the Royal Society stage The weakness of Lockyer's laboratory evidence was only too obvious to the trained chemist The Cambridge observers first gave attention to the reversal of metallic lines, then to the peculiar behaviour of magnesium especially in presence of hydrogen, to the so called carbon spectrum, to the spectrum of water finally, they studied in detail the spectra of a number of elements These inquiries were carried on over a period of more than ten years Fortunately the work is published in a collected form, it is a monument of accurate observation and of original and skilful manipulation combined with extreme caution of statement and inference Much of it is of permanent value and there is a rich store of fact in the memoirs which remain to be exploited especially, I believe, in connection with the "carbon" spectrum

Dewar did not confine his attention to spectroscopic inquiry during this period At Cambridge he instituted a series of atomic and molecular weight determinations, in the Royal Institution laboratory, where he had gradually installed a powerful electric plant, working on Deville's lines, he did much to unravel fundamental high temperature problems He was a pioneer worker on the formation of nitric oxide in the electric arc

Thus far he had done little to satisfy his artistic longing for novelty of effect he was but learning to exercise his genius

Still, a chill came upon him before he took cold, when suddenly, at the close of 1877, the scientific world was electrified by the news of the liquefaction of oxygen and hydrogen by Cailletet in France and Pictet in Geneva Such a discovery could but react on the Royal Institution, where nearly all the previous work on liquefaction of gases had been done He lost no time in obtaining the Cailletet apparatus and it was shown in operation in the Institution in the summer of 1878 The ghost of Faraday was ever about Dewar He quickly set to work and developed his appliances, limited as the funds were at his command, still, the heat engendered in spectroscopic inquiry had also to be dissipated and this was not easily done, the lust of the earlier battle being upon him

Meanwhile, two Polish physicists had extended Pictet's achievement and made notable progress Liquid oxygen was first shown in the Royal Institution in 1884 From that time onwards progress was continuous and rapid His methods have been developed and are in use the world over When Kamerlingh Onnes liquefied helium, he could operate with only 200 litres and had but 160 litres in reserve Now airships are filled with the gas. Onnes had 20 litres of liquid hydrogen ready for his first experiment and he was using the last litre when liquid helium was first "just perceived" Recently, Prof McLennan, of Toronto, describing the apparatus he has built, states that he has obtained a litre of liquid helium with the expenditure of only 10 litres of liquid hydrogen—such is progress when once the initial step is taken

Dewar's object was never merely to liquefy gases He was never the mere artificer but always the philosopher seeking to penetrate into the far-distant region of the ultimate zero of temperature All can appreciate the work of Arctic explorers like Franklin, Nansen Amundsen and Scott, the difficulties they encountered and the character of their findings Few can appreciate the work Dewer did in hyper-Arctic regions—the genius, the resourcefulness, the infinite patience that were needed to thread a way through the trackless field—the danger, too, of the work Often he carried his life in his hands and had more than one surprising escape He triumphed as an engineer and as a philosopher, though, like Scott, he had his Amundsen The story of those turbulent times must some day soon be told faithfully, to future students of the progress of science it will be in an impenetrable jungle if this be not done It is a human story, reminiscent of prescientific days, of cattle-lifting in the Highlands and of vendetta in southern climes. It has an ethical side—one on which Dewar constantly dwelt, in which the essential nobility of his character came to the fore

As to the melody and meaning of his work, what has he given to the world? Liquid air, liquid hydrogen—refrigerating agents of previously undreamt-of potency, solid oxygen, solid hydrogen, other similar conquests scarcely less notable were his too So he stands pre-eminent for all time as champion Arctic discoverer, the map of Frigor being now all but drawn As in geographical exploration, however, so in physical science, mere additions to the map are of relatively small importance, what counts most is the knowledge gained of the new territory, of its resources and of its wonders Arctic exploration proper has brought little that is specially novel to our knowledge, we have learnt most from tropic lands An explorer in hyper-Arctic regions, Dewar brought back tropic wealth

To liquefy so many gases was an astounding feat of skill To him, however, this counted as little, what counted with him was the means he gained of revelling in regions yet untrod He developed a truly marvellous technique.

First, he taught the world how to conserve cold—and heat too, if necessary—by his invention and development of the vacuum flask. Without the silvered flask little could have been done with liquid air and similar agents. The public can appreciate the value of the invention—indeed, the "Dewar flask," so we should insist on calling it, is now known to every one and used by most

A more far-reaching and original discovery, involving an astounding development of the technique of high-vacua, was that of highly-cooled "charcoal" Indirectly, Dewar was the originator of the use of charcoal, as chief absorbent material, in the gas-mask used in the war against poison gas He had shown how the absorbent properties of charcoal could be developed and raised to a maximum Various people are repeating what he did and are making no little fuss over their assumed "discoveries", Americans especially are talking big about what they are pleased to call "activated carbon'

I have said that Dewar was the virtuoso—this quality is pre-eminent in his scientific work Too many conquerors have left destruction in the path of their progress—his was always adorned with flowers, he could not help strewing them by the wayside

He studied the properties of matter at low temperatures in every direction Probably the most important of these inquiries, that, I think, which he was inclined to regard as the most illuminating, on the theoretic side, was that into the heat capacity of the elements at the boiling-point of hydrogen, about 21° absolute or −252° C He also did much work on the heat capacities of compounds which has not been published

I have no time to speak of other work on properties as influenced by temperature, such as was done in co-operation with Fleming on specific inductive-capacity or with Hadfield on the strength of metals It is full of plums for coming scientific 'little Jack Horners' Probably the results may be read, at least in part, along lines such as those suggested above

Dewar, as I have said, was always sprinkling flowers by the wayside To chemists he often threw pearls and pearls of great price. Two, in particular, I will first mention We talk constantly of the kinetic theory of gases—which is at the root of creation—but how feeble and unilluminating are our usual demonstrations Dewar simply filled a flask with vapour of brown bromine, sealed off its neck, turned it upside down and poured liquid air into the depression in its bottom hey, presto! the molecules all crowded to the cold surface and fell asleep there, seemingly dead, almost in the flashing of an eye As a visual demonstration of the kinetic theory there is nothing to equal this, though of course some imagination must be used upon it to make it appear conclusive.

Still more striking was his demonstration of the similar all-but-immediate condensation, by liquid hydrogen, of the air filling a barometer tube—the formation of an all but-perfect barometer As I have said elsewhere, the heart leapt with joy when these feats were first witnessed. The greatness of this second demonstration is not easily realised—the efforts exercised by generations of workers before it was possible Dalton, Davy, Faraday, Gay Lussac, Avogadro, Andrews, Cailletet, Pictet, Olzewski, Wroblewski, besides others, are to be mentioned as pioneer workers in this field but Dewar was in no way the least, though last, for his imaginative and constructive power was perhaps little short of equal to that of all previous workers put together The theory is now established for all time by Aston's crowning act in molecular ballistics, which has enabled him to assess the true masses of most of the known "elementary" species

Still, we have to recognise—and Dewar has shown this in many ways—that chemistry, even the chemistry of the gases, is not mere ballistics, that strange element, afflatus, call it what we may, commonly denominated love or affection —the ruling passion of our society and of the animate world—is certainly traceable back to the molecules and to their atoms Even helium, the least affectionate of known materials, shows evidence of it, if only it receive a sufficiently cold welcome from charcoal, then its innate selfishness is overcome and it mildly subsides into the cells of its black paramour, with but slight display of heat—yet sufficient to prove that the molecules are not entirely lone souls when reduced to liquidity

I have time for only one more reference—to the ozone work and to that on phosphorescent discharge I hold this to be of primary importance but the chapter is scarcely opened Dewar was a wizard At one time he would show diamond or hydrogen burning below liquid oxygen and calmly point to ozone as a constant product as an educt of the combustion of oxygen in and by oxygen At another he would unburn the oxygen molecule at the surface of the solid substance—by means of ultra-violet radiation—and demonstrate the birth of ozone triplets among the progeny Then he would demonstrate the internecine warfare set up in oxygen by an electric discharge, with the aid of the glow which attends the gradual passage, if not of ozone triplets into oxygen twins, of some recurrent oxidation effect

$$O_3 + \epsilon\delta + O_3 = O_2 + O_2 + O_2 + \epsilon\delta.$$

The glow must be an electrical phenomenon—in it, doubtless, we witness the gradual oscillatory downfall of the ozone molecules, the outward and visible sign being the "electric" glow discharge

Dewar, however, made everything phosphoresce—even feathers and paper By cooling greatly he forced the molecules to keep company, the evidence that they do so again being the "electric" discharge as they rub themselves apart.

One of Dewar's most beautiful demonstrations—I believe also specially significant—was that of the known fact, always a paradox to the chemist, that phosphorus only glows in oxygen at a particular partial pressure What is the glow? "The glow of oxidation" is the conventional reply—but oxidation of what? It has been said of a particular oxide of phosphorus, formed at an early stage. I venture to think it is the glow of the "oxidation" of oxygen—of and by ozone, in other words The interpretation may be extended, as a working hypothesis, at least, to all glow phenomena traceable to oxidation—even to the glow worm.

One other set of demonstrations I must mention Faraday, we know, always had in his mind's eye the picture of some continuum which made "induction" possible Dewar gave signal proof of the continuity of chemical change—of the need of a connecting "Faradic" link between molecules, if they were to interact—in his remarkable demonstration with a Crookes' tube containing an earth which phosphoresced when an electric discharge was rained down upon it, he but cooled the tube externally by applying a pad of wool soaked in liquid air the phosphorescence ceased The moisture within the tube is to be pictured as coming to rest, like the bromine

I can refer but briefly to the great closing act of the drama I am striving to describe The curtain is rung up upon a complete transformation scene—no longer is the attempt being made to coerce the molecules into company by freezing instead, their desire for and affection in the liquid state is brought under notice in the so-called soap film, in its final stage of black tenuity

I often tried to get his view of this state—but, to the end, he was the true experimentalist the patient student seeking to throw light upon darkness but unable to penetrate behind the veil watching the play of inter-molecular forces which are at the seat of the world's activity, he was lost in reverent wonder

A keen student of affairs and politics, he was torn with anxiety, the difficulties in the management of the Institution were very great. He was distressed also by his powerlessness to help—that he should be so entirely put aside and that his vast experience of explosives and of many other matters then of consequence should be cast to the winds An attempt was even made to deprive him of his laboratory When his services could not be dispensed with and the opportunity came to do something of which others were incapable—to develop the liquid-air metallic flask for use by aeroplane pilots—with astonishing ardour he threw himself unsparingly into the work and was happy for a time

But he ever returned to the film The only interlude was in the period during which he developed a charcoal-gas thermoscope of amazing delicacy, when he occupied himself in measuring the radiation from the sky at night Cold was used to measure cold, with the aid of a film of caoutchouc frozen stiff by the liquid air behind it—an extraordinary feat of imagination and the most refined manipulative skill With this wonderful instrument the man of nearly 80 kept lonely vigil upon the cold roof often far into the night—a worshipper of the infinite

He died at the Royal Institution in his eighty-first year, on March 27, 1923 He had been working in his laboratory until late on the night of March 20 and was taken ill in the early hours of the following morning

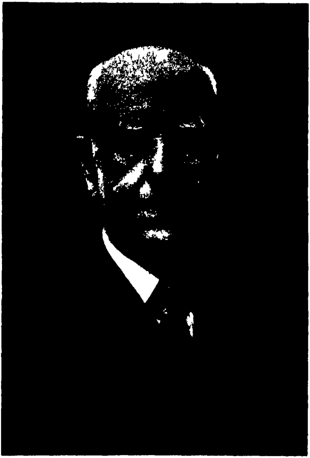
[Abridged by the Secretary from the Obituary Notice in 'Nature,' April 7, 1923, and the Friday evening lecture delivered Jan 18, 1924, at the Royal Institution by Prof. Armstrong]

SIR ARCHIBALD GEIKIE —1835-1924

SIR ARCHIBALD GEIKIE was elected a Fellow of the Society in 1865 at the age of 29 years and at the time of his death in 1924 he was the senior Fellow and hence the father of the Society Throughout this long series of years he was devotedly attached to the Society and most anxious to promote its welfare and further its activities in all possible directions and the Royal Society is much indebted to him for the services he rendered to it during the periods he acted as one of its officers He served on the Council first from 1885 to 1887 and was Foreign Secretary from 1889 to 1893 In 1903 he was elected Secretary on the biological side in succession to Sir Michael Foster and had as colleague on the physical side his friend Sir Joseph Larmor the presidents during his term of office as Secretary being Sir William Huggins and Lord Rayleigh

During the later years of the nineteenth century the work of the Society had undergone considerable expansion both on the physical and on the biological side Thus the part played by the Society in such undertakings as the International Catalogue of Scientific Literature the Association of Academies the National Physical Laboratory and the investigations into certain tropical diseases considerably increased not only the range of the activities of the Society but also added considerably to the work of the Officers Fellows and staff Geikie throughout his tenure of office took the greatest interest in the work of the Society as a whole and his outlook was always a wide one although as Secretary his activities were mainly concentrated on the biological side One of the most characteristic features of his work was the interest he took in all biological questions botanical zoological and physiological He never confined his interest to the more special branches of knowledge that he had made his own

During Sir Michael Foster's tenure of the Secretaryship and whilst Mr Joseph Chamberlain was Secretary of State for the Colonies arrangements had been made in consultation with the Colonial Office for the Royal Society to undertake the supervision and control of a series of inquiries into the causation and nature of important maladies affecting the welfare of our tropical Dominions and dependencies *e g* malaria Malta fever sleeping sickness Valuable results have been obtained by the successive commissions sent out under the auspices of the Tropical Diseases Committee of the Royal Society Geikie took the greatest possible interest in this work not only from the actual scientific interest of the questions involved and the results obtained but also from the point of view that the Royal Society in super-



Arch Geikie

vising and controlling such work for the assistance of the Government was doing work for which it was exceptionally fitted and fulfilling a most important function in promoting the welfare of the Empire

Like Foster Geikie held the view that all such work undertaken for the Government should be rigorously confined as it was to the investigation of definite scientific problems and not extended to either administrative matters or to supervising methods of medical treatment of given diseases This work often entailed a considerable burden on the Officers and Fellows of the Society and also some increase in the actual expenditure of the Society but Geikie felt that the Royal Society as the foremost scientific society should be willing to undertake such work and that it was specially fitted to carry it out to a successful conclusion On relinquishing the secretaryship to become the President of the Society he maintained the closest possible touch with the Tropical Diseases Committee and rarely missed taking the chair at its meetings Certainly the Fellows of the Society interested in physiological and pathological questions are indebted to him for the wide interest he felt in and the sympathy he extended to their investigations and work

In his anxiety that the Society should continue to hold its place as the foremost Scientific Society he was always wishful that it should contain within its ranks men distinguished in all branches of natural knowledge and more especially that it should include amongst its fellows those who had gained distinction from their researches although not following a scientific career as a profession The British Empire has long been noted for the number of men who have pursued scientific studies and gained distinction by the results achieved notwithstanding the fact that such studies have either formed their relaxation or else have been pursued solely out of the interest evoked by them Such men have often been miscalled amateurs and the Royal Society has always contained such men amongst its fellows Geikie was greatly impressed with the necessity of maintaining this custom as he was convinced that it gave the Society a breadth of view that otherwise it might not have He even went further and often regretted that the old custom of including amongst the Fellows men who had obtained distinction in walks of life other than those actually included under the term natural knowledge, was not more frequently followed He felt strongly that it was only by these means that the Society would maintain the status it was rightfully entitled to as representative of learning In this connection it may be recalled that it was during his presidency that arrangements were made whereby the recently founded British Academy was enabled to use the apartments of the Society as a meeting place

Geikie was a very efficient officer of the Society spending much time in the offices of the Society and making himself familiar with all the details of the work that falls to the lot of the officers He was a pleasant colleague to work with, and had usually clearly cut and defined views on the various questions that came up for decision by the Officers and Council, and thus the business of the Society was conducted with dispatch under his auspices

The activities of the Society have for long been somewhat hampered by the inadequacy of the funds at its disposal, and Geikie, like other Presidents of the Society, often alluded in his addresses and public utterances to the necessity of more liberal endowments if the Society was to fulfil its functions in the advancement of natural knowledge It was a source of gratification to him in his last years that several munificent benefactions were received by the Society, thereby enabling it to endow Research Professorships in several branches of Science

Geikie not only made himself familiar with other branches of Science outside the range of his own speciality, but, in addition, he had a well-developed literary and artistic side His literary ability is well seen in his numerous writings dealing with a considerable variety of subjects, some biographical, several relating to his beloved Scotland, *e g*, Scottish Scenery and Scottish Reminiscences, and several classical, more especially relating to Roman family life, Horace's villa, etc He was at one time fond of sketching, especially amidst the Western Isles, and the present writer well remembers the graphic manner in which he described these scenes, and how he had wished to follow the career of an artist to place them on canvas For many years he was in the habit of yachting on the West Coast of Scotland, and was familiar not only with the scenery, but also with the folk-lore and traditions of the islanders He had a fund of Scottish stories and was an admirable raconteur, telling his stories with a keen relish of their humour. Many of them may be found in his well known Scottish Reminiscences

The 250th Anniversary of the foundation of the Royal Society was celebrated in 1912 during his tenure of the presidency, and he not only took the greatest interest in the various ceremonies and functions that marked the anniversary, but also played a very active part in the work of the Officers and staff in making all the arrangements necessary for the celebration Further, the Society is indebted to him for compiling and editing a new and enlarged edition of the Record of the Royal Society, and it was at his instigation that a facsimile of the ancient Charter Book was prepared Geikie took a very special interest in all that concerned the life of the Royal Society in the past, and one of the best illustrations of this and of his literary activities is to be found in the history of the Royal Society Club that he published in 1917, after he had relinquished the presidency of the Society, under the title of the Annals of the Royal Society Club This is a very complete and accurate history of the doings of the club from its foundation in 1743 up to the year 1902, and contains much information of the manners and customs of the times and many anecdotes illustrating the characteristics of some of the more prominent of the early Fellows of the Society Geikie was a member of the club from 1890 to his death, and was a very constant attendant and a great believer in the humanising influence of social meetings especially those of a dining club with such ancient traditions as those of the Royal Society Club

Geikie received the honour of Knighthood in 1891 and that of K C B in 1907 and in 1913 the Order of Merit was conferred on him and he also became Officier de la Légion d'Honneur

Geikie married on August 10th 1871 Alice Gabrielle Anne Marie Pignatel who died on January 21st 1916 His family consisted of one son Roderick who died on December 6th 1910 and three daughters one of these died on February 23rd 1915 Sir Archibald Geikie died on November 10th 1924

J R B

The scientific career of Sir Archibald Geikie was one of great distinction Joining the Geological Survey in 1855 he became Director General of the Geological Survey of the United Kingdom in 1882, President of the Geological Society London 1890 92 and was selected by the Council of that Society for a second term of office to preside at the Centenary Celebrations in 1907 Honours were showered upon him by scientific societies at home and abroad and by Universities these were crowned by the award of the Order of Merit in 1914

Born in Edinburgh in 1835 and educated at the High School and University, he derived inspiration from the classic surroundings the scene of the fierce controversy between the Huttonians and Wernerians at the beginning of last century His finding of fossils in the Burdiehouse limestone in his boyhood marked the first stage in his field experience He roamed over Arthur's Seat and the Pentland Hills with Charles Maclaren's volume on 'The Geology of Fife and the Lothians' as his guide Not content with excursions in the neighbourhood of Edinburgh he went to Arran with Ramsay's account of the geology of that island in his hand to examine the metamorphic rocks and palæozoic strata pierced by the granite masses in the north of the island. This expedition was followed in his eighteenth year by a visit to Skye where he began the mapping of the Lias in the district of Strath after a careful study of Macculloch's volume on The Geology of the Western Islands

All these excursions sprang from his own initiative They showed that he was clearly destined for a geological career if such could be obtained Two articles which he wrote on his work in Arran secured an introduction to Hugh Miller then living in Edinburgh which led to a close friendship that lasted till the tragic end of Hugh Miller's career The young geologist paid frequent visits to that home with his specimens his maps and notes receiving in return great encouragement to continue the work Soon after this introduction Hugh Miller was asked by Sir Roderick Murchison who had been appointed Director General of the Geological Survey to recommend a young geologist to carry on the mapping in East Lothian, begun by Professor Ramsay in 1854 Archibald Geikie was recommended and he joined the staff in his twentieth year

He made the acquaintance of other scientific men in Edinburgh at that time, who were impressed with his enthusiasm for geological research Dr George Wilson, Lecturer on Chemistry in the extramural school and Director of the Science and Art Museum, in whose laboratory he did chemical analyses followed his early progress with great interest Robert Chambers, Professor Fleming, one of the able naturalists of that period, and Professor James David Forbes, whose work among the glaciers of the Alps and Norway is familiar to geologists, befriended him Forbes who was Secretary of the Royal Society of Edinburgh for twenty years, appealed to him to contribute papers to the Society, for he regretted the decline of geological research in Scotland since the days of Hutton, Hall and Playfair Archibald Geikie responded cordially to this appeal in later years by communicating his best papers to this Society

From the point of view of worldly advancement, Murchison was his greatest benefactor In 1860, after a few years' experience of field work in the lowlands, the young geologist was requested by Murchison to accompany him in the North-west and Central Highlands to determine the order of succession of the rocks in those regions From these traverses arose an intimate friendship, which lasted till the close of Murchison's life in 1871 Through Murchison's influence he was appointed first Director of the Geological Survey in Scotland in 1867 When Murchison offered to share the endowment of the new Chair of Geology in Edinburgh University, he stipulated with the Government that Archibald Geikie should be the first Professor

The areas fixed by Professor Ramsay, then Director of the Geological Survey of Great Britain, to be mapped by Archibald Geikie in his early official career, gave him great gratification His colleague was H H Howell, a coal field expert, and after completing the survey of the low ground in the county of Haddington, they moved westward to Midlothian To Geikie was assigned the area west of the coalfield, ranging from Arthur's Seat and the Pentland Hills to the Bathgate Hills, and northwards into Fife His experience in those areas determined the lines of research in which he did his best work The evidence bearing on the glaciation of the region, the development of the Old Red Sandstone formation in the Pentland Hills, and the occurrence of volcanic rocks on different geological horizons, suggested fields of investigation that might bear rich fruit

In his early survey days, in common with the prevalent opinion of that time, he attributed the polishing and grooving of the rocks to the action of currents and icebergs, but under the influence of Professor Ramsay, who had already described the vanished glaciers of North Wales he adopted the view, propounded by Agassiz during his visit to Scotland in 1840, that these phenomena were due to the action of land ice In 1862 he contributed to the Glasgow Geological Society a valuable paper on 'The Glacial Drift of Scotland' (published in

1863) which helped to place the investigation of these deposits on right lines He showed how the rock striations radiated from the main mountain ranges he described the local character of the boulder clay its relation to the underlying rocks the direction of transport of the materials its striated pavements the intercalated deposits of sand and gravel —observations which have stood the test of time From these phenomena he inferred that during the earlier part of the glacial period Scotland was covered with an ice sheet after the manner of Greenland that the boulder clay was a product of this ice sheet and that the stratified beds in the Till marked periods of lessened severity of climate when the ice retired for some distance He described the inland stratified drift and the fossiliferous marine shelly clays of the Clyde basin so admirably worked out by Smith of Jordanhill He suggested that the moraines in the upland valleys indicated the gradual shrinkage of the ice-sheet into local glaciers and the final disappearance of the ice

Availing himself of the researches of Smith of Jordanhill Edward Forbes T F Jamieson and others he appended to this paper a list of organic remains from the glacial deposits of Scotland

This paper proved of great service to British geologists at that time as it gave an outline of the conditions which probably prevailed during the glacial period in this country and suggested the lines along which investigation should proceed It held the field till the publication in 1871 of the well known volume 'The Great Ice Age by his younger brother Professor James Geikie

As the Scottish survey work advanced it fell to the lot of Archibald Geikie to map in detail large areas of the Old Red Sandstone in Midlothian Lanarkshire Ayrshire and in the counties of Fife Perth and Kinross He also examined the districts surveyed by other members of the staff south of the Grampians Throughout this region it had been proved that this formation consisted of two divisions an upper and lower separated by a marked unconformability and characterised by different fish faunas

North of the Grampians however Murchison adopted a triple classification by introducing a middle division composed of the Caithness flagstones From their lithological characters and fossil contents he maintained that this flagstone series belonged to a different division of the formation He argued that the fish fauna found in this series differed in important points from that occurring in the flagstones sandstones and shales of Lower Old Red Sandstone age in Forfarshire It was therefore of younger date He also suggested that the Caithness flagstones might have been laid down during the long interval separating the lower and upper divisions south of the Grampians

Hugh Miller and Dr Malcolmson had proved the occurrence of the upper division with its characteristic fish remains in the basin of the Moray Firth and they further showed that the ichthyolites found in the lower beds in that region resembled those met with in the flagstones of Caithness and Orkney

Such was the position of enquiry when Geikie began a series of traverses in the basin of the Moray Firth Caithness Orkney and the Shetland Isles In 1878 he communicated to the Royal Society of Edinburgh an elaborate paper on the Old Red Sandstone of Western Europe which embodied the results of these traverses It was intended to be the first of a series descriptive of the other areas occupied by this formation in the British Isles but his removal to London in 1882 prevented him from carrying out this intention The other areas were dealt with at a later date in his treatise on the Ancient Volcanoes of Great Britain with special reference to the records of volcanic action associated with them

One of the special features of this communication is the vivid description of the geographical changes in Western Europe that followed the marine conditions of Silurian time Adopting the theory of the lacustrine origin of the Old Red Sandstone suggested by Fleming and Godwin Austin and supported by Rupert Jones on palæontological evidence and by Professor Ramsay on lithological grounds he held that in North West Europe the Silurian sea gave place to continental conditions with large inland lakes He defined the areas of the various basins of deposit of the Old Red Sandstone in the British Isles and gave them the following names —(1) Lake Orcadie including the extensive region north of the Grampian range and stretching north to the Shetland Isles (2) Lake Caledonia or the Mid Scottish Basin between the Grampian Highlands and the Southern Uplands (3) the Lake of Lorne extending from the south east of Mull to Loch Awe (4) Lake Cheviot including a part of the south east of Scotland and north of England (5) the Welsh Lake bounded on the north by the Cambrian and Silurian high grounds its southern and eastern extension being obscured by later formations

The deposits in Lake Orcadie were grouped by him in two divisions a lower comprising the Caithness flagstone series and an upper composed of false bedded sandstones and marls with its characteristic fish fauna resting uncomformably on the lower as in the midland valley of Scotland He pointed out that Murchison s lower division in Caithness consisted merely of the thick accumulation of sandstones breccias and conglomerates that underlie the Caithness flagstone series

The distinctive feature of the paper was his correlation of the Caithness flagstone series (Murchison s middle division) with the true Lower Old Red Sandstone south of the Grampians He admitted the marked differences in the lithological characters and fossil contents of the deposits in the two areas but he contended that the palæontological distinctions are probably not greater than the contrast between the ichthyic faunas of adjacent but disconnected water basins at the present time

Much new information bearing on the distribution and field relations of these deposits was embodied in this communication The main features in the geological structure of Caithness were indicated, the great overlap at Reay in the north of that county where the higher members of the flagstones rest unconformably on the crystalline schists, was clearly established, his suggestion that the fish-bearing bands and associated strata in the Moray Firth basin are the equivalents of part of the higher portion of the Caithness flagstone series has been confirmed by the later detailed mapping of the Geological Survey He also recorded for the first time the unconformability between the Upper Old Red Sandstone and the Caithness flagstones visible on the west coast of the island of Hoy, Orkney

In accordance with his classification the Caithness flagstone series and associated strata were grouped with the lower division of the system in the official publications of the Geological Survey But after his retirement from the Survey, the palæobotanical evidence threw new light upon the problem The researches of Dr Kidston and Mr P Macnair showed that the assemblage of plants found in the Caithness flagstones differed from those met with in the Lower Old Red Sandstone south of the Grampian Chain, and ought to be referred to a middle division The triple classification based upon the plants harmonised with that advanced by Dr Traquair, based upon the fishes The value of this evidence was appreciated by the Geological Survey in 1902 and the three-fold grouping of the system has been adopted in the official publications since that date

Turning now to volcanic geology we enter a sphere of research in which Archibald Geikie laboured with great success This branch of geological enquiry roused his enthusiasm, and led him to study volcanic phenomena in the British Isles and other lands As his knowledge of volcanic activity in different geological periods increased, he showed great aptitude in modifying his opinions in accordance with fresh evidence

In mapping the areas assigned to him in Mid-Lothian, West Lothian and Fife in his early official life, he frankly acknowledged his obligations to the clear descriptions of Charles Maclaren, whose work was far in advance of its time These descriptions proved the occurrence of volcanic action in Old Red Sandstone and Calciferous Sandstone time His own field work in the Bathgate Hills showed that volcanoes were active at intervals during the Carboniferous Limestone period on higher horizons than those of the Arthur's Seat volcano He recorded the prevalence of later intrusive dykes traversing the Carboniferous strata From his own researches and the work of other investigators, he prepared a paper on the "Chronology of the Trap Rocks of Scotland," published in the 'Transactions of the Royal Society of Edinburgh' in 1861 In the map illustrating this communication the Trap Rocks are referred to the Old Red Sandstone, Carboniferous, Oolitic and Tertiary periods In accordance with the classification of Edward Forbes, the extensive basaltic plateaux of the West Highlands were assigned to the Jurassic period, except the lavas at Ardtun, in Mull, which are associated with the well-known leaf beds described by the Duke of Argyll This grouping was corrected in an important paper that appeared in the 'Proceedings of the Royal Society of

Edinburgh in 1867 in which he suggested that the basaltic plateaux, extending from the North of Ireland along the West Coast of Scotland to the Faroe Islands and Iceland were all erupted probably during the Tertiary period Even at that date he emphasised the importance of the system of intrusive dykes which in his opinion was possibly the most striking manifestation of Tertiary volcanic activity

While mapping the volcanic area in Fife between Burntisland and the Saline Hills he visited the Auvergne in Central France with its extinct but recent volcanoes to increase his knowledge of volcanic phenomena In 1868 he visited the volcanic district of the Eifel in Germany and in 1870 at the request of Poulett Scrope author of the well known volume on Geology and Extinct Volcanoes of Central France he undertook an examination of the volcanic districts of Southern Italy and the Lipari Islands He was impressed by the contrast between the comparatively low craters of the Phlegraean Fields where the eruptive materials consist mainly of tuffs with few lava flows and the great crater wall of Monte Somma whose lavas are piled on each other to a great height and pierced by innumerable vertical dykes filling fissures made at successive eruptions An attack of malarial fever prevented him from carrying out his intention of examining the Lipari Islands

Another stage in his pursuit of the study of volcanic phenomena in Scotland is marked by an important paper contributed to the Royal Society of Edinburgh in 1879 on the Carboniferous Volcanic Rocks of the Firth of Forth Basin—their Structure in the Field and under the Microscope

As his field work proceeded in the Lothians and Fife he felt the necessity of applying the microscope to the study of the igneous rocks in order to gain definite knowledge regarding their internal composition and structure He realised that much new light might be thrown on the history of volcanic action in this region by this field of enquiry

In his historical sketch he notes with pleasure that the igneous rocks of the Edinburgh district furnished Hutton with the evidence whereby he established the igneous origin of whinstone (basalt) and led to the famous experiments of Hall which laid the foundations of experimental geology

The volcanic masses were grouped by him in four sub-divisions (1) Necks or Vents (2) Intrusive Sheets and Dykes (3) Contemporaneous Lavas (4) Tuffs A notable feature of this communication was the prominence given to the numerous necks or vents occurring in the Lothians Fife and Stirlingshire, from which proceeded showers of ashes and sheets of lava Most of them were regarded as belonging to different stages of Lower Carboniferous time while others were supposed to be later than the folding and faulting of the Carboniferous sediments and were referred to the Permian period The occurrence of these vents and their wide distribution is one of the valuable contributions made by Archibald Geikie to Scottish volcanic geology

In the petrographical part of this paper he acknowledges Allport's researches on the Carboniferous dolerites round Edinburgh and gives an outline of his own investigations. Subsequent petrographical work has shown that he did valuable pioneer work in this branch of inquiry, for he was the first to describe many important features of the microscopic characters of these rocks.

Archibald Geikie's discovery of proofs of volcanic action during Permian time in Scotland is of special interest. While mapping the Mauchline district in Ayrshire he recorded a series of contemporaneous lavas and tuffs underlying the Permian sandstones of that region and forming a ring of higher ground between the Carboniferous and Permian sediments. This discovery was announced in the Geological Magazine in 1866. Similar types of lava were mapped by him in the Thornhill basin in 1868, where they are also associated with Permian sandstones. He laid special emphasis on the occurrence of volcanic necks in excellent preservation in Ayrshire, which he referred to this period. Some of the smaller ones rise through the ring of Permian lavas, while others occur in the upper division of the Coal Measures. They are filled with agglomerate, pierced in some cases by igneous intrusions.

In describing the volcanic phenomena of Permian age, he suggested that the great series of volcanic vents in East Fife probably belonged to this period. He also suggested that the coarse agglomerates of the Arthur's Seat volcano and the associated igneous rocks, which in his opinion marked a second period of volcanic activity, were probably erupted during Permian time. But the subsequent detailed mapping of the Geological Survey led him to accept Maclaren's later interpretation, confirmed by Professor Judd, that these coarse agglomerates occurred within the vent from which the lavas and tuffs of the hill had been discharged during one period of volcanic action in Lower Carboniferous time.

Another great opportunity of extending his knowledge of volcanic phenomena occurred to Archibald Geikie in 1879. He had arranged to give a course of lectures at the Lowell Institute, Boston, in the autumn of that year, and he resolved to spend the summer in traversing the extensive lava fields drained by the Snake River in Idaho on the Pacific slope of the United States. The vast floods of lava in that region, with no visible cones and craters, were explained by Richthofen as being due to fissure eruptions. Hitherto Geikie had regarded the Scottish volcanic plateaux as having issued from local vents, but this visit widened his conceptions. The great lava plain looked as if it had been filled with molten rock which had kept its level and wound in and out along the bays and promontories of the mountain slopes as a sheet of water would have done. The Snake River has cut a gorge through this plain which exposes a succession of sheets of basalt to a depth of several hundred feet. No central cone from which these lavas might have been erupted was visible; only a few cinder cones of secondary origin appeared at wide intervals on the basaltic plain The suggestion then occurred to him that the Tertiary volcanic plateaux of Western Europe might have had a similar origin

Inspired by this conception, he revisited the West Highlands at intervals for several years to continue his investigations among the Tertiary igneous rocks He was also impelled to do so by the remarkable interpretation of the volcanic history of that region advanced by Prof Judd In a paper communicated to the Geological Society on 'The Ancient Volcanoes of the Highlands' in 1874, Prof Judd described the basal wrecks of five great extinct Tertiary volcanoes (Skye, Mull, Rum, Ardnamurchan and St Kilda) the one in Mull was estimated by him to have reached a height of 14,500 feet They indicated three periods of volcanic activity The first was marked by the extrusion of acid lavas and tuffs connected with plutonic masses of granite, the second by basaltic lavas and tuffs related to deep seated masses of gabbro, and the third by the discharge of lavas from small sporadic cones after the great central volcanoes had become extinct

At last, after a quarter of a century of intermittent labour in this subject, Archibald Geikie presented, in 1888, to the Royal Society of Edinburgh his great memoir on 'The History of Volcanic Action during the Tertiary Period in the British Isles' In the preparation of this monograph he acknowledges the assistance he received from several of his colleagues A prominent feature of it is the elaborate description of the system of basic dykes, the importance of which he recognised early in his career His main conclusions may thus be briefly summarised

Owing to enormous horizontal tension a series of more or less parallel fissures arose in Tertiary time in a tract of country, including the north of England and Ireland, the southern half and the west coast of Scotland —a total area of about 40,000 square miles Molten material rose up these fissures, thereby giving rise to the numerous basic dykes which are the distinctive feature of the volcanic region The basalt plateaux are supposed to be due to streams of lava issuing from these fissures and from vents occurring along these lines of weakness After these sheets of lava had accumulated to a great thickness, they were injected by laccolitic masses of gabbro, and sills and veins of dolerite At a later period the gabbros and basalt lavas were alike disrupted and pierced by acid igneous rocks, ranging from granites and granophyres to porphyries and felsites Crustal movements again ensued whereby another series of fissures was established, now filled with basic dykes that traverse alike the basalt plateaux, the later gabbros granophyres and granites

It is interesting to observe that these main conclusions were confirmed by Dr. Harker in the course of his detailed mapping of the central mountain group of Skye for the Geological Survey But from the recent exhaustive memoir issued by the Geological Survey on the 'Tertiary and Post-Tertiary Geology of Mull, Loch Aline and Oban,' it is evident that the volcanic history of Mull is much more complicated than Sir A Geikie or Professor Judd imagined Mull is regarded as a volcanic centre of extreme complexity which 'has repeatedly served as a focus of fissure eruptions , but it is doubtful whether the lavas still spared by erosion are not in the main, the products of a central volcano, an idea always linked with the name of Professor Judd

His last contribution to this branch of geology was his comprehensive treatise on the Ancient Volcanoes of Great Britain which appeared in 1897 It presented a summary of the knowledge then ascertained regarding these volcanoes, and embodied the results of his own researches and of others who had worked at volcanic problems in the field and in the laboratory It traversed a wide field of enquiry for the opening chapters of the treatise are devoted to the discussion of the general principles and methods of investigation of volcanic phenomena which are followed by detailed descriptions of the proofs of volcanic activity in Britain ranging from pre Cambrian to Tertiary time

In the traverses with Murchison in the North West and Central Highlands in 1860 Archibald Geikie had to deal with problems of fundamental importance connected with the geology of the Highlands The researches of Macculloch, Murchison and Sedgwick, Hay Cunningham and Hugh Miller showed that the belt of quartzites and limestones in the West of Sutherland and Ross are succeeded eastwards by metamorphic rocks that stretch across the Great Glen to the eastern border of the Highlands Accepting Salter s determination of the fossils found in these limestones by Mr C W Peach, Murchison regarded these strata as Silurian (now known to be Cambrian by Mr A Macconochie s discovery of the *Olenellus* fauna in the Fucoid beds) He contended that these Silurian strata pass *conformably* below and are overlain by, the metamorphic rocks to the east and inferred that *this metamorphic series* must belong to the same system This interpretation meant a radical change in the geological map of Scotland for the area occupied by these altered strata amounts to about 11,000 square miles

Professor Nicol, on the other hand maintained that no conformable upward succession from the fossiliferous limestones and associated strata to the over lying schists is to be found He held that the line of junction is a line of fault everywhere indicated by proofs of fracture, contortion of the strata and powerful igneous action "

It fell to the lot of Archibald Geikie to traverse rapidly with Murchison the line of junction in the county of Ross where, owing to stupendous inversions and overthrusts, the prevalent dip of the fossiliferous strata and the Eastern Schists is towards the east south-east He was misled by the apparent super position and especially by certain deceptive sections in which the Eastern Schists rest with similar dip and strike upon the undisturbed Silurian rocks Eventually he accepted Murchison's interpretation

The results of these traverses were embodied in a joint paper communicated to the Geological Society, London in 1861, 'On the Altered Rocks of the Western Islands of Scotland, and the North Western and Central Highlands'

Murchison's interpretation of the structure was therein described and illustrated by sections in such convincing form that it met with general acceptance for many years

In 1878 the controversy was reopened, and Murchison's position was shown to be untenable by several investigators Dr Hicks, Prof Bonney, and Dr Callaway made important contributions to the problem

Prof Lapworth grasped the true solution of the geological structure of that region In 1883 he began a series of articles in the 'Geological Magazine on ' The Secret of the Highlands, based on his detailed mapping of the Durness Eireboll region in 1882, but owing to severe illness this series was never completed He therein demonstrated the inversion of the Silurian strata on the east side of Loch Eireboll and the unconformable junction of the basal quartzite with the old Archæan floor on the east side of the fold at Ant Sron From his paper on The Close of the Highland Controversy ('Geol Mag,' 1885) and from the Obituary Notice of Charles Lapworth,' by Prof Watts and Sir Jethro Teall ('Proc Roy Soc,' 1921), it is clear that he recognised that the Archæan Gneiss had been driven over the fossiliferous quartzites on Ben Arnaboll by a gently inclined overthrust fault Along this plane of movement and at other localities, the original rocks had been crushed and rolled out into types which he termed mylonites On the shore at Heilim, on the east side of Loch Eireboll, he observed that the serpulite grit had been repeated many times by clean-cut faults a striking illustration of imbricate structure All these phenomena were shown in the field in 1883 to Sir Jethro Teall by Prof Lapworth

The Durness Eireboll region was mapped by Peach and Horne in 1883-84, when they reached conclusions practically identical with those of Prof Lapworth regarding the stratigraphy and metamorphism of the rocks, in complete ignorance of his results (see "Close of the Highland Controversy,' p 98 'Geol Mag 1885) It was then proved in the course of the geological survey work that under extreme lateral pressure the rocks behaved like brittle, rigid bodies, they snapped and were driven westwards in successive slices, so that crystalline gneiss and schist are made to rest upon fossiliferous strata of Silurian age It was further shown that the Eastern Schists were driven westwards by the Moine thrust—the most easterly and most powerful of the series—for a minimum distance of ten miles over all underlying thrust masses, till they rest directly upon the Silurian (Cambrian) limestone in the Durness basin

The evidence proving these conclusions was carefully inspected in the field by Archibald Geikie, who had never had an opportunity of examining the Eireboll sections He was completely convinced that Murchison's interpretation of the structure must be abandoned, and he took the earliest opportunity of making a public declaration to this effect A report giving the results of the work by Peach and Horne, with a preface by Geikie containing a frank confession that he had been misled and that he had accepted the conclusions of his colleagues appeared in Nature November 13th 1884

In dealing with the geological structure of the Silurian rocks of the Southern Uplands he accepted the order of succession adopted by Nicol and Murchison and was largely influenced in holding this opinion by the doctrine of Colonies This theory was introduced by Barrande the distinguished palæontologist to explain the intercalation of fossils belonging to higher zones in lower portions of the Silurian succession in Bohemia These precursory fossiliferous bands were termed Colonies The distribution of the bands of graptolite shale in the Southern Uplands as mapped by the Geological Survey was regarded as an instance of the precursory appearance of the higher graptolite forms in the Moffat region and their disappearance in the Lead Hills district

But the researches of Prof Lapworth furnished the key to the solution of the structure of the Chain He demonstrated a definite faunal sequence in the graptolites which is persistent though the strata may be inverted by folding He further proved a great variation in the character of the contemporaneous sedimentary deposits the black shales of the Moffat region ranging from Arenig to Llandovery time about three hundred feet in thickness being represented in the Girvan area by several thousand feet of sedimentary deposits

Reference must be made to his tenure of the Chair of Geology for eleven years in Edinburgh University By his lectures which were given in a clear and attractive form and especially by his class excursions he was an inspiring teacher Edinburgh is an ideal centre for practical training in field geology but in addition at the end of each session he carried out a long excursion lasting a week or ten days to examine special problems in the field Receptive students who took part in these excursions felt the influence of his personality He thus describes the impression produced on one of his former students by these practical demonstrations

' These students rambles and the love of geology which they fostered have dwelt ever since those days in Sir William Herdman s memory and though he has become eminent in another field of natural science he has assured me that it was the remembrance of his experience in the Geology Class at Edinburgh and its excursions which led him in recent years to found and endow a Professorship of Geology in the University of Liverpool It is not always that a teacher lives to see the fruition of his labours Certainly no incident connected with my professional career has given me keener pleasure than this generous liberality of a former student

Archibald Geikie s eminent services as an exponent of geological science in his class books and text books demand special mention His experience in the field during his early official career enabled him to test the truth of the principles laid down by Hutton and illustrated by Playfair regarding the evolution of the earth s surface features The potency of the ordinary agents of denudation in hollowing out valleys was not admitted by some of the leading geologists of that time Even Sir Charles Lyell who was the great exponent of the uniformitarian school contended towards the close of his career that the principal valleys in almost every great hydrographical basin have been due to other causes besides the mere excavating power of rivers

Geikie was an ardent follower of the views of Hutton and Playfair He was impressed with the remark of Desmarest when pointing out the value of Hutton s contributions to the natural history of the earth and the physical geography of Scotland It is to Scotland that Hutton s opponents must go to amend his results and substitute for them a more rational explanation Geikie was convinced that Scottish topography furnished no grounds for such opposition He produced in 1865 his volume on The Scenery of Scotland viewed in Connection with its Physical Geology which gave an excellent popular description of the Huttonian principles of earth-sculpture as illustrated by the country he knew best He showed with great clearness and artistic style how the ordinary agents of denudation—rain rivers the sea the wind and moving ice acting upon different types of rock had carved out the distinctive varieties of Scottish scenery As the volume was based on personal acquaintance with the physical features of the country and a knowledge of its geological structure then ascertained it immediately arrested attention Its success was marked it ran through three editions the later editions incorporating the more important advances in Scottish geology

In view of the success of this volume he then projected a series of educational works on Physical Geography and Geology to meet the public demand In 1873 he contributed to Macmillan s elementary science series a primer on each of these subjects a task which cost him excessive labour His aim in writing the Physical Geography Primer was to stimulate habits of observation of the common phenomena of every-day experience It ranks as one of his best educational achievements These primers were followed by class books on the same subjects for which there has been a great demand The great educational value of these publications is beyond doubt Their success is due to his teaching being permeated with the Huttonian conceptions of natural forces now in operation and to the exquisite literary form in which the lessons are presented

These primers and class books were meant to be the precursors of his great Text book of Geology the first edition of which appeared in 1882 This volume was intended for the use of students and professional workers in the science and so well did it meet the requirements of the time that the whole issue was disposed of in a comparatively short period One of the valuable features of the book was his analysis of the research done in other countries in each of the great divisions of the geological record It reflected extensive reading and the careful preparation of brief summaries of the results achieved He made a strenuous effort to keep each successive edition abreast of the research of the time and in dealing with his own record he frankly abandoned positions which he had previously held when new evidence proved that they were erroneous The fourth edition, published in 1903, after his retirement from the Survey, is notable for copious references to the geological literature of other countries, which cost him enormous labour It is also notable for the qualification which he attached to Huttonian teaching, as he thought uniformitarianism had been pushed too far

"It has often been insisted upon that the Present is the key to the Past, and in a wide sense this assertion is eminently true While, however, the present condition of things is thus employed, we must obviously be on our guard against the danger of unconsciously assuming that the phase of nature's operations which we now witness has been the same in all past time For aught we can tell, the present is an era of quietude and slow change compared with some of the eras that have preceded it"

A reprint of the fourth edition of the text-book was issued in 1924

His active brain and fertile pen enabled him to produce several biographies in the midst of other onerous labours He completed the 'Life of Edward Forbes,' begun by Dr Wilson, he wrote the 'Memoirs of James David Forbes,' of Murchison, of Ramsay, who succeeded Murchison as Director-General of the Geological Survey The Life of Murchison is of permanent interest to geologists from his vivid sketches of the Founders of Geology in Scotland and England, and from his description of the achievements of Sedgwick and Murchison in establishing the Cambrian, Silurian and Devonian systems

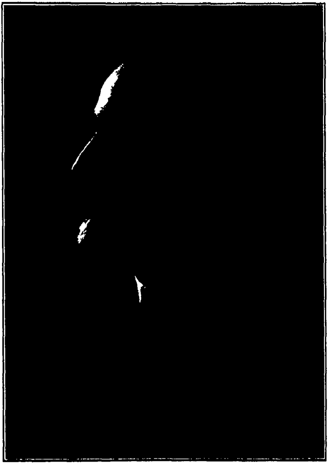
J H.

EDWIN HENRY BARTON—1858 1925

Colleagues of Prof Barton who met him during the late summer of 1925 saw in him the fine figure of a man apparently in robust health brimful of energy both mental and physical and with the prospect of many years of undiminished activity before him His most intimate relations and even he himself were equally in happy ignorance of any cause of trouble and yet on September 23rd having just returned from a holiday in North Wales spent in walking and climbing as was his wont he died without a moment's warning—a tragic but not unhappy ending to a life of strenuous endeavour crowned by no mean success Nearly one half of his lifetime was spent in a grim struggle to get his foot on the first rung of the ladder of distinction This once accomplished although his circumstances permitted him for the first time to enjoy some of the simple pleasures of life there seemed to be but little relaxation of his efforts His subsequent continuous rise in his profession and his happy family relationships must however have made the second half of his lifetime in glowing contrast to the first—a period of increasing satisfaction and joy

Edwin Henry Barton was born in Nottingham in 1858 his father died young and his mother was left to battle alone to keep herself and her three children This commencement of his career under conditions of such poverty that he was obliged to leave school and earn something towards his own living must of course have had a great influence on his outlook on life and on his prospects Most ordinary boys of his age would have regarded freedom from book work as some compensation for his changed position Barton however whether spurred on by ambition urged by his devout mother or guided by a natural liking for study denied himself the usual pleasures of boyhood and devoted all his spare time to the improvement of his education

In those days there was little encouragement to or opportunity for a youth to attend evening classes but the opening of the University College of Nottingham in 1881 provided Barton then a man of 23 with facilities which he eagerly grasped Entering the College as an evening student immediately after its doors were opened so well did he use his opportunities that in the course of some years he passed the London Matriculation and Intermediate Science examinations The bare statement of such elementary successes is not impressive but in the case of one who had been taken from school at an early age and whose energy was absorbed by daily toil such achievements were a proof of exceptional industry determination and self-denial During the whole of this period the absence of all trivial pleasures from Barton's life may be inferred the delights of cricket football and all other games were unknown



E. H. Barton

to him An engineer's employé by day, a student by night, at the age of 32 his youth was passing or had passed, and although his sterling qualities had raised him from a junior position in a drawing office to that of chief draughtsman, he had not yet embarked on his real life's-work But the tide in his affairs, which ultimately led him to fame, was now reaching its flood Having saved a little money, he determined to give up his occupation as a draughtsman and to become a day student of the University College in order to pass the London B Sc examination This aim he accomplished, taking 2nd Class Honours in Physics after one year's work, and shortly afterwards he was granted an 1851 Exhibition The tide had turned He was now launched on his career as a man of science Under Prof Rücker at the Royal College of Science, London, and then, under Prof Hertz in the University of Bonn he commenced his training in research work On his return from Germany in 1893 he was appointed Junior Demonstrator in Physics under Prof W H Heaton in University College, Nottingham, two years later, having meanwhile taken the London University D Sc degree, he was made a Senior Lecturer in the Physics Department, and finally in 1906 he was appointed to the Chair of Experimental Physics

During the 32 years in which he was engaged in teaching, his published research work gradually raised him from obscurity to a high position in the scientific world That his work was of very great value was proved by his election to the Fellowship of the Royal Society in 1916, a coveted honour, so difficult to obtain, especially by a provincial Professor, who has few opportunities of making himself known except in print The poor, self-educated youth who entered the Nottingham College in 1881 thus took his position among the leading physicists of his day He had brought credit and distinction to the institution which had helped him to rise, his example and his teaching encouraged many of his students to devote themselves to science Between him and his colleagues the most cordial relationships invariably obtained in all matters of academic work, always kindly, genial, and ready to help others, his influence was of the best, but his lack of sympathy with all games a result of his studious boyhood-prevented him, perhaps, from establishing those numerous comradeships which come so easily to the average Briton who engages in outdoor sports Barton's tastes were less combative, he was interested in sound, not only as a theoretical physicist and as the author of a well known "Text Book of Sound," but also as a player of many kinds of musical instruments, he was also a lover of nature, fond of his garden and of the country-side He married at the age of 35 and left two sons, both of whom, as rising physicists, bid fair to follow in their father's footsteps

His first two papers, the result of work with Hertz in the Bonn laboratory, were published in the 'Proceedings' of the Royal Society and dealt with electrical interference phenomena somewhat analogous to Newton's rings, but exhibited by high frequency waves passing along parallel wires with short circuited ends and containing portions which cause partial reflexion All his other publications appeared in The Philosophical Magazine commencing with a series (1897 1900) on the absorption of electric waves by a terminal bridge on their attenuation and their reflexion at the oscillator and on the reflexion and transmission by condensers of electric waves along wires

His researches hitherto had been inspired by his early work with Hertz but in 1901 Barton began to turn his attention to the subject on which he became so great an authority namely that of acoustic and other mechanical vibrations The first result was a theoretical paper on the refraction of sound by wind this was followed by several others on the practical investigation of the air pressures used in playing brass instruments and of the relations between the vibrations of a string and those which consequently occur in the bridge sound box and contained air of the instrument on which the string is mounted The mathematical treatment of the lateral vibration of bars and of the spherical radiation and vibrations in conical pipes in 1908 was followed by another series of important practical and theoretical studies of the vibration curves of violin strings and of the belly and bridge of the instrument and also of the air therein contained with the aid of optical levers fixed on the bridge or other more lively parts of the belly he magnified the vibrations and recorded them on a photographic plate He also carried out a mathematical and experimental study of the range and sharpness of resonance under sustained forcing and their variations with pitch the results of which rendered clearer many points in the theory and practice of brass instruments A suggestion made by Eccles at the British Association meeting in 1912 that the bending of the waves round the earth in long-distance wireless telegraphy is due to a higher velocity of propagation in the upper regions of the atmosphere owing to the ionization there present led Barton to an experimental investigation of this possibility although his results did not settle the question they favoured rather than disfavoured Eccles views This work however only interrupted for a short time his researches on acoustics and other vibrations to which he returned in 1917 In that year he commenced with Miss Browning the experimental investigation of the vibrations of coupled—or of double-cord—pendulums and the results illustrated many important points in the phenomena of inductively-coupled electric circuits The joint authors then passed on to the study of double-cord pendulums in which the masses of the bobs or else the lengths of their suspensions were unequal—systems which were somewhat analogous to coupled electric circuits with different inductances or different periods The results obtained when the masses of the bobs and the periods of the separate vibrations were both unequal were also investigated This work led to the experimental study of forced vibrations which play an important part in many branches of physics A single heavy driving pendulum was first used to actuate a number of light ones of graduated lengths, all suspended from the same tightly-stretched cord Following up this idea a similar set of pendulum "resonators" was employed to show the effects on them of two simultaneous harmonic forcings of different periods The photographic records which were obtained enabled the authors to assert that their results were nowhere in conflict with the resonance theory of audition, and that it was quite unnecessary to assume the existence of a larger number of separate vibrators and nerves than are actually present in the human ear

The conception of tri-colour vision due to Young, and developed by Helmholtz and Maxwell, was then studied in a similar manner with a system of three-light pendulums, the effects of stimulus on these responders being photographically recorded and compared with the facts of colour vision The conclusion arrived at was that with corresponding mechanisms actually present in the retina, "colour vision would be in the main as we now find it"

In 1912 papers on "triple pendulums with mutual interaction and the analogous electrical circuits" were followed by others on the dampings of pendulum vibrations, in which it was shown that the relations between viscosity and damping could be employed for the comparison and determination of the viscosities of liquids In his last paper, published in November, 1925, he returned again to the study of musical instruments, and analysed with the aid of photographic records the sound changes of the trumpet and cornet

F S K

WILLIAM JAMES LEWIS—1847-1926

It was with considerable surprise that his Cambridge friends and colleagues learned, towards the close of the Easter vacation, of the death of the University Professor of Mineralogy, on April 16, at the home of his sister Mrs G T Pilcher, Treen, Godalming Surrey For although he had more or less recently suffered from attacks of bronchitis, he had made good recoveries, and there appeared every prospect of his well-known excellent constitution asserting itself for some years to come Yet, after a slight further indisposition and when he had apparently quite thrown it off, he was found to have died during a rest in his room at Treen, probably from heart failure, and in a manner which seems to have been peaceful and painless He was in his eightieth year, having been born on January 16, 1847, the second son of the Rev John Lewis, at Llanwyddelan in Montgomeryshire He had occupied the Chair of Mineralogy at Cambridge for 45 years, and had been a Fellow of Oriel College, Oxford, for exactly 57 years -surely a combination of service in both the ancient Universities which is rare if not unique

As a boy, William J Lewis was educated at Llanrwst School, and thence went up to Jesus College, Oxford, the training ground of so many distinguished Welshmen, as a scholar in October, 1865 Here he took up especially mathematics and natural science, and obtained first classes in Mathematical Moderations in 1867 in the Finals in 1868, and in Natural Science in 1869, finishing this portion of his career by his election in April, 1869, to a Fellowship at Oriel, and by winning the Senior Mathematical Scholarship in 1871

During the years 1870 and 1871, however, he was an assistant master at Cheltenham College, where he taught mathematics and natural science, so that his Oriel Fellowship dates practically from 1872 Now he was greatly interested in the lectures of Prof Nevil Story Maskelyne while at Oxford, and being attracted by the fame of W H Miller, the Professor of Mineralogy at Cambridge since 1832 the father of modern crystallography, whose method of describing crystals is still unsurpassed and universally current, he went to Cambridge in 1874 to study under that famous crystallographer He afterwards studied mineralogy for several months at the University of Bonn, and on returning in 1875 obtained an appointment at the mineral department of the British Museum, then at Bloomsbury, under his former teacher, Nevil Story Maskelyne, who was then acting as keeper of the minerals Two years later, in 1877, serious lung trouble developed, and he wisely resigned the position, being succeeded by Sir Lazarus Fletcher, and proceeded to warmer climates abroad. This step proved to have been taken just in time, for his health became eventually quite restored It was during this enforced absence from England that he accom-

W. J. Lewis

panied two solar eclipse expeditions, and carried out the observations of the polarization of the corona which were published in the Royal Astronomical Society's Solar Eclipse Volume

In 1879 Lewis returned to Cambridge, and acted as Miller's deputy during the latter's illness He was incorporated as a member of Trinity College, and after sojourning for a time in outside lodgings was given rooms in College, and resided there for the rest of his life In February, 1881, he was elected to succeed Miller, who had died after holding the Chair of Mineralogy for nearly fifty years, 1832–81 This professorship had been founded in 1808 the first occupant of the chair having been Dr E D Clarke In 1822 the latter was succeeded by J S Henslow, who, six years later, in 1828, was followed by the celebrated Master of Trinity, William Whewell, who, however only occupied the chair for four years, until 1832, when Miller succeeded him and elaborated the Millerian System of Crystallographic Notation, which had already been suggested by Whewell, to whom the conception is fundamentally due It was first worked out in its present form and detail, however, by Miller, and published in his 1839 'Treatise on Crystallography"

In the year 1876 the Crystallological Society was founded, with Lewis as its secretary, and he continued to hold the honorary post until 1883, when the Society was amalgamated with the Mineralogical Society He became Librarian of the Mineralogical Society in 1890, the library being housed in the New Museums at Cambridge, and was President of the Society during the three years 1909–12 In 1909 he was also elected a Fellow of the Royal Society

In 1884 Lewis inaugurated a most useful Scholastic Agency in Cambridge, as a private venture, long before the official Appointments Board was formed or thought of, and numerous young university men have owed their start in the hard life of the world, on leaving the 'Varsity," to this paternal institution, which was devised by its kindly founder for this especial purpose It was rendered even more valuable by being combined with an insurance scheme on particularly favourable terms, the advantages of which were entirely on the side of the student

The collection of minerals at the New Museums, Cambridge, is one of very considerable interest, both intrinsically and historically, and was much enlarged during the long period of Lewis's occupancy of the chair Not only was he constantly adding to it the results of his many visits to the mineral districts of the Alps, especially the Binnenthal, but it was notably enriched by the purchase of the Joseph Carne collection, and by the gift during his lifetime by the Rev Dr Thomas Wiltshire, formerly Professor of Geology and Mineralogy at King's College, London, of a fine collection acquired during many years by him.

During one of the later of these mineral hunting expeditions in the Alps, in the summer of 1919, when seventy two years old, Lewis went out alone one afternoon from the little hotel at Binn for a stroll to the Langenbach quarry As he did not return for the evening meal a search party went out to seek him just before darkness fell but were unable to find him Next morning about ten o clock some villagers at work near the quarry heard shouts and eventually discovered him sitting near the edge of the quarry with a broken leg The quarry was half filled up with old snow and ice and about three o clock in the afternoon Lewis was standing on some of it when it suddenly gave way and he found himself largely buried in it with a mass of ice pinning down one of his legs which it had broken and with a still larger mass threatening to fall on his head and chest if he made the least movement So there he lay all night unable to make anyone hear his calls for assistance the search party having taken the wrong direction With truly wonderful endurance he kept his head and consciousness and in the early morning after the night s freezing had more or less fixed the threatening ice masses he gradually managed to free his leg and although it was badly broken to crawl out of danger and to bind on to it a splint improvised from a tree branch lying fortunately within reach and then to crawl to the edge of the quarry from which he was eventually able to attract the attention of the working party He was then got down to the inn where the leg was roughly set Eventually he was taken to a hospital at Berne where the leg had to be again broken and reset and where he had to remain many weeks In the end however he made a perfect recovery

As regards his scientific writings Lewis is chiefly known by his book A Treatise on Crystallography published by the Cambridge University Press in 1899 in the Cambridge Geological Series It is essentially a mathematical and geometrical textbook of crystal morphology and from this point of view is *still pre eminent* The subject of *crystal twinning* is especially well treated for Lewis was quite an exceptional authority on crystal twins His original memoirs consist of two (his earliest) published in the Journal of the Chemical Society in 1875 concerning the crystallographic characters of organic substances three in the Proceedings of the Cambridge Philosophical Society in 1882 and 1883 six later ones in the Philosophical Magazine and ten in the Mineralogical Magazine (Proceedings of the Mineralogical Society) They are mostly descriptions of new characters or occurrences of known minerals and of organic substances and inorganic salts But three others call for special mention The first concerned The Analysis of the Rhombohedral System " a paper read before the Crystallological Society in 1878 and was important as offering a better geometrical method of dealing with rhombohedral crystals The second was a paper to the Cambridge Philosophical Society in 1882 on The Measurement of a Bead of Platinum by the late Prof Miller and is noteworthy from the fact that it records that Miller had in 1874 constructed a two-circle goniometer (which is still in the mineralogical laboratory at Cambridge)—thus long before its more recent so-called invention by Fedorov in

1889 and, independently, by V Goldschmidt in 1893 and its use by the V Goldschmidt school —and had used it in the autumn of 1874 to measure the facets on this more or less spherical bead of fused and recrystallized platinum, by a theodolitic method The notes left by Miller were put together and interpreted by Lewis in the 1882 paper in question The third memoir is one of 1898, read to the Mineralogical Society, on ' Some Twins of Calcite and a Simple Method of Drawing Rhombohedral Crystals, and of Deducing the Relations of their Symbols," the nature of which is well indicated by its title, and further illustrates the two lines of work, twinning and rhombohedral geometry, to which Lewis specially devoted himself

In April, 1906, Lewis was in Italy, and was present at the great eruption of Vesuvius from the 7th to the 12th of that month, the period of greatest violence, and has left a manuscript giving a vivid description of the wonderful and terrible phenomena as seen both from Naples and from the actual slopes of the mountain, together with sketches of the scene at various times and measurements of the great pillar and cauliflower- or umbrella shaped cloud above the crater The height of the pillar varied from 2 2 to 2 7 times the height of the mountain, and the top of the cauliflower he gives as no less than 4 6 times the height of the mountain Naples streets were inch-deep in ash-dust He ascended several of the actual lava streams and measured their width and rapidity of advance The great cauliflower cloud he describes as brightly ruddily illuminated below by the red-hot lava, and above by the continuous lightning, while the repeated ejection of lapilli was each time like the simultaneous discharge of thousands of rockets Moreover, the terrible roaring of the mountain and the rattle of the falling stones were blended with the incessant peals and rollings of the thunder, the whole forming a veritable inferno of terrifying grandeur and magnificence

Besides his scientific publications, Lewis wrote a book on " The History of the Parish of North Wraxhall, Wilts, with a Life of the late Rector Francis Harrison " (published by the S P C K in 1913), the latter being for many years a close friend and also a Fellow of Oriel It is an interesting work which, obviously, entailed much historical and antiquarian research, includes some good stories of the old days at Oriel, and shows Lewis in an altogether new light He was, indeed, capable of forming a few great friendships, and when he endowed a scholarship at Oriel he attached to it the name of his friend, Francis Harrison Notable instances of further friendships were those with the late Sir Lazarus Fletcher, Henry Jackson, the former Vice-Master of Trinity and Regius Professor of Greek, and Sir James Frazer, O M , another Fellow of Trinity

Still another side of Lewis's character was his affection for, and great kindness to, children, and no more sincere mourners of his loss were present at his funeral than two little boys and their mother (the war widow of the grandson of another old friend, Dr Harper, Fellow and Principal of Jesus College, Oxon), who had spent many happy play hours at tea parties with their kind old host in his rooms at Trinity.

Lewis was never married, and, one of the last of the Fellows of the old régime, he was at his death much the Senior Fellow of Oriel. It was fitting, therefore, that his funeral, on April 20, should take place at Oxford, the service at Oriel, and the interment at Holywell Cemetery. There was also a Cambridge memorial service at Trinity on April 28.

Perhaps no better indication of Lewis's kindliness and generous thought for others could be afforded than to mention in concluding this notice, that while spending his long night's vigil after his accident in Switzerland, immovably wedged between blocks of ice and with a broken leg, he elaborated a plan for scholarships at Bedford College, the details of which he wrote to his sister, Mrs. Pilcher, the next day after his rescue. Moreover, he actually carried out his scheme by founding three of them, for the daughters of Welsh clergymen, and coupled them with the name of his little never forgotten nephew, Lewis Pilcher, who died as the result of an accident some years ago. His friends in the Mineralogical Society will also remember the effective, yet tactful, manner in which he led and organized the very timely temporary aid afforded to Belgian colleagues during the war, and to the aged Prof. Victor von Lang, a former colleague at the Mineral department of the British Museum, in the evil days of Austria just after the armistice. Moreover, during the war he returned his salary as professor to the University. All this, however, was merely the expression of Lewis's nature, and it is this impression of him which will render his memory honoured and ever green to those who knew him best.

A. E. H. T.

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